CHARACTERIZATION OF DEGRADATION PRODUCTS OF ACTIVATED DIETHANOLAMINE AND METHYLDIETHANOLAMINE DURING CARBON DIOXIDE ABSORPTION AND DESORPTION PROCESSES

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“CHARACTERIZATION OF DEGRADATION PRODUCTS OF ACTIVATED DIETHANOLAMINE AND METHYLDIETHANOLAMINE DURING CARBON DIOXIDE ABSORPTION AND DESORPTION PROCESSES”

ABSTRACT

Degradation studies of activated Diethanolamine (DEA) and Methyldiethanolamine (MDEA) induced by carbon dioxide were conducted in jacketed glass reactor under absorber and stripper conditions at atmospheric pressure. Piperazine (PZ) is used as an activator in this system. There are eighteen amines and activated amine samples studied. Pure carbon dioxide was bubbled through the reactor till saturation. The concentration of amine and activator used ranging from 2M to 4M and 1M to 2M respectively. On the other hand activated amine concentrations ranged from 4M to 11M. Six generic cycles were conducted for each run during the degradation experiments. Each cycle configured with the absorption and desorption of carbon dioxide at 55 ˚C and 100 ˚C respectively. Samples were collected after a predetermined experimental time and analyzed by various chromatographic methods to identify degradation products. The degradation products were identified using ion chromatography (IC), high performance liquid chromatography (HPLC)-UV detection and gas chromatography mass spectroscopy (GC/MS). In the IC analysis three different columns were used for Anion, Cation and Ion exclusion systems these are Metrosep A Supp 5 150/4.0, Metrosep C Supp 4 150/4.0 and Metrosep Organic Acids respectively. The supelco HPLC column was used to identify polar degradation products of amine sample. In the GC-MS chromatographic analysis HP-INNOWAX (30 m × 0.250 mm × 0.25µm) column was used. The major identified degradation products in IC analysis are nitrate, nitrite, acetate, phosphate and ammonium. In HPLC analysis the most common degradation products are found formamide, 2-(2-aminoethoxy)ethanol, Diethylenetriamine, Ethyl 1-piperazinecarboxylate, N-(2-Hydroxyethyl) ethylenediamine, Triethanolamine, 2-Methoxyethanol, Ethylene glycol, 1,4-Dimethylpiperazine and 1-(2-Aminoethyl) piperazine. GC-MS is particularly conducted for five alkanolamine samples which are DO2PZ2M, D05DEA4M, D10DEA7MPZ2M,

D13MDEA4M and D18MDEA7MPZ2M. Five degradation products are identified for DO2PZ2M and these are Formamide, Ethylenediamine, N-formylpiperazine, Fomic acid and Imidazole. D05DEA4M degraded sample shows ten degradation products these are Formamide, *N*-(hydroxyethy1) ethylenediamine, Oxazolidone, 2-(2-aminoethoxy) ethanol, 2-amino-2-methyl-1-propanol, *N*,*N*-bis(hydroxyethy1)- ethylenediamine, Ethylurea, 2-methylaminoethanol, ethanol and acetone. Activated DEA sample D10DEA7MPZ2M shows twelve DGPs these are Formamide, 1,4-Bis(2-hydroxyethyl)piperazine, Oxazolidone, 1,4-Dimethylpiperazine, *N*,*N*-bis(hydroxyethy1)ethylenediamine, 2-dimethylaminoethanol, 1-(2-Aminoethyl)piperazine, Ethyl-1-piperazinecarboxylate, Acetic acid, Glycolic acid, Ethyl urea and Acetone. Inactivated MDEA samples D13MDEA4M was analyzed and eleven degradation products are found which are 1, 4-Bis (2-hydroxyethyl)-piperazine, Bis-(2-hydroxypropyl) amine, Oxazolidone, 2-(2-aminoethoxy)ethanol, 2-Amino-2-methyl-1-propanol, 2-dimethylaminoethanol, Ethylurea, Glycolic acid, Acetaldehyde, Ethanol and Acetic acid. Similarly eight degradation products are found for D18MDEA7MPZ2M sample which are 1-Methyl piperazine, 1, 4-Bis(2-hydroxyethyl)piperazine, Bis(2-hydroxypropyl) amine, N, N-dimethyl piperazine, 2-Amino-2-methyl-1-propanol, 2-dimethylaminoethanol, 1-(2-aminoethyl) piperazine and ethanol. In addition two physical properties density and viscosity of eighteen activated and inactivated amine samples are measured at 30 ˚C, 55 ˚C and 100 ˚C and it was found that the both physical properties decreased with increasing temperature. However, in case of increasing concentration it is significantly increases the density and viscosity of both activated and inactivated amine solutions.

Keywords: Degradation, activated diethanolamine, activated methyldiethanolamine, absorption, stripping, desorption

“PENCIRIAM PRODUK DEGRADASI DISKTIFKAN DIETHANOLAMINE DAN METHYLDIETHANOLAMINE SEPANJANG PROSES CARBON DIOKSIDA PENYERAPAN DAN NYAHPENYERAPAN”

ABSTRACT TRANSLATED IN BAHASA MALAYSIA

Kajian degradasi Diethanolamine (DEA) dan Methyldiethanolamine (MDEA) yang diaktifkan berikutan kehadiran karbon dioksida telah dijalankan di dalam reaktor kaca yang saluti cecair penyejuk di bawah keadaan ‘absorber’ dan ‘stripper’ pada tekanan atmosfera. Dalam sistem ini, Piperazine (PZ) telah dipilih sebagai bahan pengaktif. Terdapat 18 tahap kepekatan amina dan sampel amina yang telah diaktifkan yang dikaji dalam kajian ini. Karbon dioksida tulen telah dipam masuk ke dalam reaktor sehingga tepu. Kepekatan amina yang digunakan berada diantara 2M kepada 4M manakala kepekatan pengaktif berada dalam lingkungan 1M kepada 2M. Sebaliknya, kepekatan amina yang diaktifkan yang digunakan adalah dari 4M kepada 11M. Enam kitaran generik telah dijalankan untuk setiap cubaan dalam eksperimen. Setiap kitaran dikonfigurasi dengan penyerapan dan nyahpenyerapan karbon dioksida pada suhu 55 ° C dan 100 ° C masing-masing. Sampel-sampel dikumpulkan selepas tamat masa eksperimen yang telah ditetapkan dan dianalisis dengan pelbagai kaedah kromatografi untuk mengenal pasti produk degradasi yang belum diketahui. Produk degradasi telah dikenal pasti menggunakan ‘Ionic Chromatography’ (IC), ‘High Performance Liquid Chromatography’ (HPLC) berpengesanan UV dan ‘Gas Chromatography-Mass Spectrometry’ (GC / MS). Dalam analisis IC, tiga kolum yang berbeza telah digunakan untuk sistem ‘Anion’, ‘Cation’ dan ‘Ion Exclusion’ iaitu Metrosep A SUPP 5 150/4.0, Metrosep C SUPP 4 150/4.0 dan Metrosep Asid Organik masing-masing. Supelco HPLC kolum telah digunakan untuk mengenal pasti produk degradasi berkutub dalam sampel amina. Dalam analisis kromatografi GC-MS, kolum HP-INNOWAX (30 m × 0,250 mm × 0.25μm) telah digunakan. Produk degradasi utama yang dikenal pasti dalam analisis IC adalah ‘nitrate’, ‘nitrite’, ‘acetate’, ‘phosphate’ dan ‘ammonium’. Dalam analisis HPLC, produk degradasi yang paling kerap ditemui merupakan ‘formamide, 2 - (2-aminoethoxy) ethanol’, ‘diethylenetriamine’, ‘Ethyl 1-piperazinecarboxylate’, ‘N-(2-Hydroxyethyl) ethylenediamine’, ‘Triethanolamine, 2-Methoxyethanol’, ‘Ethylene glycol’, ‘1,4 – dimethylpiperazine’ dan ‘1 - (2-Aminoethyl)

piperazine'. Kajian menggunakan GC-MS dijalankan untuk lima sampel 'alkanolamine' iaitu DO2PZ2M, D05DEA4M, D10DEA7MPZ2M, D13MDEA4M dan D18MDEA7MPZ2M. Lima produk degradasi telah dikenal pasti untuk DO2PZ2M dan ini adalah 'Formamide', 'Ethylenediamine', 'N-formylpiperazine', 'Fomic acid' dan 'Imidazole'. Sampel D05DEA4M yang telah didegradasi menunjukkan 10 produk degradasi iaitu 'Formamide', 'N-(hydroxyethy1) ethylenediamine', 'Oxazolidone', '2 - (2-aminoethoxy) ethanol', '2-amino-2-methyl-1-propanol', 'N, N-bis (hydroxyethy1) – ethylenediamine', 'Ethylurea', '2-methylaminoethanol', 'ethanol' dan 'acetone'. Sample DEA yang telah diaktifkan iaitu D10DEA7MPZ2M menunjukkan 12 degradasi produk iaitu 'Formamide', '1,4-Bis (2-hydroxyethyl) piperazine', 'Oxazolidone', '1,4-Dimethylpiperazine', 'N, N-bis (hydroxyethy1) ethylenediamine', '2-dimethylaminoethanol', '1 - (2 - aminoethyl) piperazine', 'Ethyl-1-piperazinecarboxylate', 'acetic acid', 'Glycolic acid', 'Ethyl urea' dan 'Acetone'. Sampel MDEA yang tidak diaktifkan iaitu D13MDEA4M dianalisis dan 11 produk degradasi telah dijumpai iaitu '1, 4-Bis (2-hydroxyethyl)-piperazine', 'Bis (2-hydroxypropyl) amine', 'Oxazolidone', '2 - (2-aminoethoxy) ethanol', '2-Amino -2-metil-1-propanol', '2-dimethylaminoethanol', 'Ethylurea', 'Glycolic acid', 'Acetal dehyde', 'Ethanol' dan 'Acetic acid'. Begitu juga lapan produk degradasi yang dijumpai untuk sampel D18MDEA7MPZ2M iaitu '1-Methyl piperazine', '1, 4-Bis (2-hydroxyethyl) piperazine', 'Bis (2-hydroxypropyl) amine', 'N, dimethyl piperazine N', '2-Amino-2-methyl -1-propanol', '2-dimethylaminoethanol', '1 - (2-aminoethyl) piperazine' dan 'ethanol'. Di samping itu, ketumpatan dan kelikatan 18 sampel amina yang diaktifkan dan tidak diaktif disukat pada suhu 30 ˚ C, 55 ˚ C dan 100 ˚ C dan didapati bahawa kedua-dua sifat fizikal berkurangan dengan peningkatan suhu. Tetapi dalam keadaan peningkatan kepekatan, peningkatan ketara diperhatikan bagi ketumpatan dan kelikatan amina yang diaktifkan dan yang tidak diaktifkan.

Kata Kunci: Degradasi, diethanolamine yang diaktifkan, methyldiethanolamine yang diaktifkan, penyerapan, pelucutan, penyahserapan

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DEDICATION

To my almighty Lord who has given me the ability to do research in this University (UM), my loving parents and all Teacher, Your support and encouragement has guided me and I am forever grateful.

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DGP	Degradation Products
[DGP]	Concentration of Degradation Products
I	Initial
F	Final
α	Loading
ppm	Parts per million
L	Lean
R	Rich
RT	Retention Time
PL	Peck Level
TP	Total Number of Peaks
IC	Ion Chromatography
VS	Virgin Solution
pH-Vs	pH of Virgin Amine Solution
pH-Ls	pH of Lean Amine Solution
pH-Rs	pH of Rich Amine Solution
Act.	Acetate
AICM	Anion IC Method
CICM	Cation IC Method
OICM	Organic Acid IC Method
Std.	Standard
VLC	Very Low Concentration
TNP	Total Number of Peaks
HSS	Heat stable salts
EG	Ethylene glycol
TEA	Triethanolamine
PZ	Piperazine
MEA	Monoethanolamine
THEED	Triethylenediamine
HEI	Hydroxyethylimidazolidone
MEA	Monoethanolamine
AMP	Aminomethyl propanol
DGA	Diglycolamine
HEP	Hydroxyethyl piperazine
BHEED	*N*,*N*-Bis(hydroxyethyl)ethylnediamine
DIPA	Di-isopropanolamine
DEA	Diethanolamine
BHEP	*N*,*N*-Bis(hydroxyethyl)-piperazine

HEOD	Hydroxyethyl-oxazolidone
HEI	Hydroxyethyl-imidazolidone
THEED	*N*,*N*,*N*-Tris(hydroxyethyl)ethylenediamine
BHEI	*N*,*N*-Bis(hydroxyethyl)imidazolidone
DEAC	Diethanolamine carbamate
MEAC	Monoethanolamine carbamate
DEADTCS	Diethanolamine dithiocarbamate
AEEA	Aminoethylethanolamine
DEA	Diethanolamine
MDEA	Methyldiethanolamine
NG	Natural gas
HEIA	1-(2-Hydroxyethyl)-2-imidazolidinone
HEEDA	Hydroxyethyletylenediamine
LPG	Liquid petroleum gas
DGA	Diglycolamine
BHEEU	*N, N*-Bis(hydroxyethoxy-ethyl)urea
BHEETU	*N, N*-Bis(hydroxyethoxy-ethyl)thiourea
HPMO	Hydroxypropylmethyloxazolidone
TMPDA	*N*,*N*,*N*′,*N*’-Tetramethylpropylenediamine
TMBDA	*N*,*N*,*N*′,*N*′-Tetramethylbutylenediamine
PMDETA	*N*,*N*,*N*′,*N*′,*N*″-Pentamethyldiethylenetriamine
PMDPTA	*N*,*N*,*N*′,*N*′,*N*″-Pentamethyldipropylenetriamine
TMEDA	*N*,*N*,*N*′,*N*′-Tetramethylethylenediamine
NMR	Nuclear magnetic resonance
GC-MS	Gas chromatography mass spectrometer
GC	Gas chromatography
HPLC	High performance liquid chromatography
IC	Ion chromatography
FT-IR	Fourier transforms infrared resonance spectrometer
HPLC-UV	High performance liquid chromatography-Ultraviolet detector
CE-DAD	Capillary electrophoresis-Diode array detect

CHAPTER 01

INTRODUCTION

CHAPTER 01: INTRODUCTION

Acid gases, mainly H_2S and CO_2, are components in a variety of gas mixtures including natural gas, synthesis gas, flue gas, and refinery streams. H_2S needs to be completely removed from gas streams due to its toxicity and corrosiveness in refinery operations. Carbon dioxide removal from flue gas is a necessary means of combating global warming. Carbon dioxide is also removed from natural gas because it acts as a diluent, increasing transportation costs and reducing the heating value of the gas. Amine-based absorption/stripping with aqueous alkanolamines offer a competitive approach for capturing carbon dioxide (CO_2) from coal-fired power plant flue gas (Lu, B-. H. et al., 2012). The process of separating acid gases from source gases is referred to as acid gas treating. Industrially the most important alkanolamines are MEA, DGA, DEA, DIPA and MDEA. However, a major problem associated with chemical absorption using alkanolamines or alkanolamines blends is degradation through irreversible side reactions with CO_2 and O_2 which leads to numerous problems with the process: solvent loss, foaming, fouling, increased viscosity and corrosion. This chapter gives an overview of CO_2 emission sources and the problems associated with these emissions. Information on the traditional absorption/stripping process is given including information on solvent degradation. Finally, the research background, scope and objectives of this current project are discussed.

1.1 Global Warming and Carbon Dioxide Emissions

Global warming results from the effect of what is called the 'greenhouse effect'. Carbon dioxide (CO_2), methane, water vapor, nitrous oxide and ozone are the main greenhouse gases. The main purpose of a greenhouse is to allow sun's radiation (heat) to enter the enclosure easily, however, does not allow the heat to be radiated back to the atmosphere. Similar to a greenhouse, our atmosphere allows the sun's radiation to heat the Earth and slows down the radiated heat to go back into the space. This greenhouse effect is essential to sustain life on Earth. Now, due to the increased level of greenhouse gases, the atmosphere's ability to

trap and hold the heat increases more than required. As a result, the average temperature of the earth increases and this natural phenomenon is known as 'global warming'. It is also defined as a sustained increase in the atmosphere that causes abnormal climate change (Egmond, S. V. & Hekker, M. P., 2012). In the following description about global warming and carbon dioxide, a brief explanation regarding effects of global warming and CO_2 emission in the atmosphere, has been provided. Power plants are the major contributors to the increased level of carbon dioxide emissions in the atmosphere (Mercader, F. D. M. et al., 2012). The plants work for generating electricity by burning fossil fuels in a massive scale, which produces large amounts of CO_2. Coal is known to be responsible for about 93% of the emissions in the power plants. Natural gas produces 80% less carbon per unit of energy than coal, and hence so much of impact on the environment results in the ever-increasing pace of global warming (Kaveh, N. S., Wolf, K- H., Ashrafizadeh, S. N., Rudolph, E. S. J., 2012). Vehicles Gasoline-burning engines produce about 20% of carbon dioxide emitted in the atmosphere. The present carbon dioxide emission rate in Malaysia day by day is increasing. The recent information of CO_2 emission in Malaysia is high, at present the country occupied 30^{th} biggest position in the world on the basis of CO_2 emission. The latest information was found the Malaysia is the 30 biggest countries in the world on the basis of CO_2 emission. The CO_2 emission in 2010 in Malaysia is 123603 metric ton per capita. In 2007 the rate was higher than 2010, the position was 25 over 213 countries in the world.

1.2 An Overview of CO_2 capture and sequestration methods

There are two different types of scenarios for CO_2 removal from flue gas that are usually discussed, pre-combustion and post-combustion capture (Davison et al. 2001). Pre-combustion capture refers to gasifying a fuel with O_2 to form a syn-gas of CO and H_2. The CO can easily be converted to CO_2 and removed from the H_2 before the combustion process, since the syn-gas is produced at high pressure. This type of process is most commonly associated with a coal gasified power plant, or integrated gasification combined cycle (IGCC) power plant. Post-combustion CO_2 capture involves various methods of removing the CO_2 from the flue gas at the end of the power plant cycle. This type of removal method is generally associated with a retrofit of a pulverized fuel (coal) power plant with flue gas desulphurization (PF+FGD) or a natural gas combined cycle (NGCC) power plant. A fourth type of power plant is generally discussed, which is a modification of the PF+FGD design. Instead of burning coal with air, this plant uses pure O_2 with recycled CO_2 to control the temperature of the boilers (CO_2/O_2). While producing pure O_2 is expensive, the CO_2 recycle gives a significant concentration increase in the flue gas, which can reduce the cost of post-combustion CO_2 capture.

Several methods of post-combustion CO_2 capture are currently being developed. The most common technologies are cryogenics, membranes, adsorption, and aqueous absorption/stripping (Davison et al. 2001; IEA 1999; 2003). Cryogenic separation of CO_2 is generally only used for gas streams with high concentrations of CO_2. Due to the cold temperatures of the cryogenic solvents, the gas stream must be dehydrated, which is costly when treating the large gas volumes associated with power plant flues gas. Additionally, the cost of refrigeration is high in these processes and makes the economics of cryogenic CO_2 capture unsuitable for a flue gas application. It is difficult to achieve a high purity CO_2 product with membrane separation of flue gas without extensive process modifications like recycles and multiple stage separations.

This would lead to increased costs associated with re-compression of the flue gas and large capital investments, making membrane separation an unsuitable technology. Adsorbents are solids, such as zeolites or activated carbon that selectively binds CO_2 from the flue gas. The adsorbent beds are regenerated by either applying heat to liberate the CO_2, temperature swing adsorption (TSA), or by reducing the pressure to allow the CO_2 to desorb from the solid, pressure swing adsorption (PSA). The heat duty associated with TSA is large and PSA requires pulling a vacuum on the adsorbent bed or compressing the flues gas prior to the CO_2 separation step. Additionally, current adsorbents are limited by low selectivity and poor CO_2 capacity (Davison et al. 2001). The final method of post-combustion capture is aqueous absorption/stripping. The amine based absorption and stripping system were described in the following with solvent degradation.

1.3 Aqueous alkanolamine based absorption and stripping process

The process of separating acid gases from source gases is commonly referred to as Gas treating, Acid Gas Removal, or Gas Sweetening. H_2S and CO_2 concentrations in gas streams vary from several parts per million to 50% by volume. Clean-up specifications also vary widely depending on the process and the nature of impurity**.** Aqueous absorption and stripping is currently the only technology that is developed enough for commercial application of CO_2 capture from flue gas. In a typical gas sweetening unit, prior to entering the amine absorber, the acid gas will normally pass through a separator to remove solids and liquids from the gas. In some units wash water is circulated to increase the removal of solids and entrained liquid from the gas to avoid potential foaming in the absorber. The separator is usually equipped with baffles and a mist extractor (eliminator), which traps the liquid entrained in the gas before it leaves the vessel. The sour gas is then fed to the absorber where it is contacts with the lean amine solution.

Absorption followed by reaction between acid gas components will take place. Reacted amines, normally known as “Rich Amine”, will be regenerated in amine regeneration unit which is called regenerator or stripper. The absorber is normally a tray column with bubble caps on each tray for good liquid-gas contact. Packing column or mix of packing and tray are also used for this purpose. The sour gas enters the bottom of the absorber at a temperature between 40-60 ^{o}C and rises upwards through the bubble caps while the lean amine enters at the top of the contactor and flows downwards. In order to prevent condensation of hydrocarbon, the lean amine temperature is kept at 10 ^{o}C warmer than the sour gas temperature. Fig. 1.1 shows a schematic diagram of the amine sweetening process for CO_2 capture.

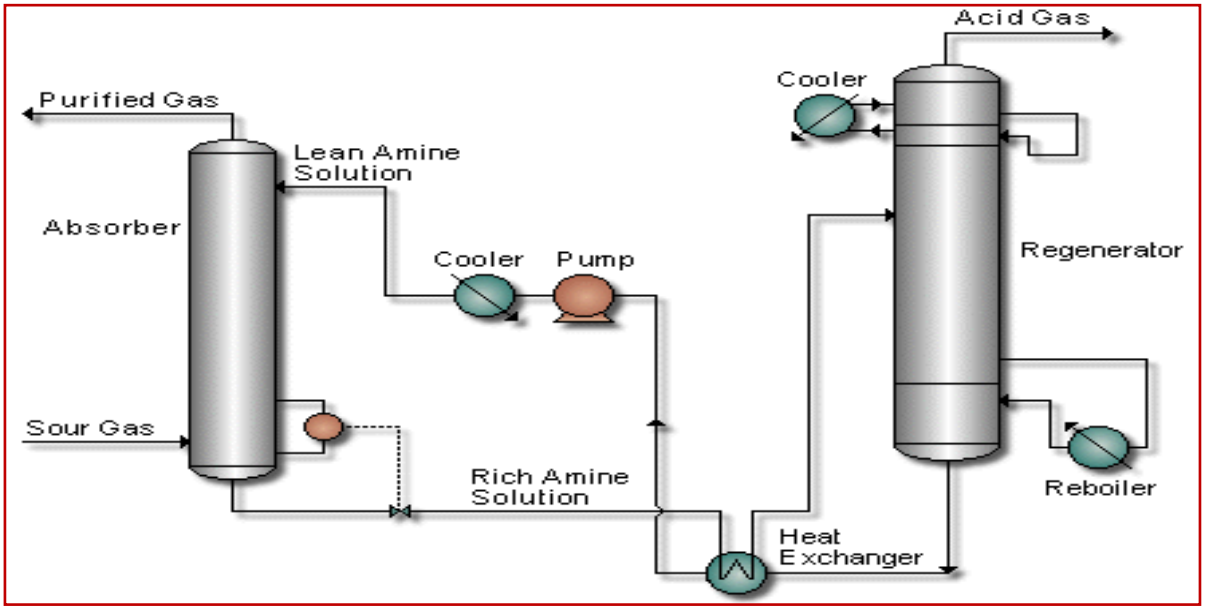


Figure 1.1: Simplified absorption/stripping system

After removing the CO_2 from the flue gas it must be permanently stored to ensure it will not be released to the atmosphere. The two methods of sequestration are either ocean storage or geological sequestration. Geological storage is currently accepted as the best sequestration method, which includes storage in depleted oil and gas reservoirs, deep saline reservoirs, and unminable coal seams (Davison et al. 2001). Injecting CO_2 into depleted oil and gas reservoirs can enhance the recovery of oil and gas by 10-15%.

This technique, enhanced oil recovery (EOR), is an established technique but not widely in use today. Injection of CO_2 into unminable coal seams also recovers methane that is adsorbed on the coal. Deep saline aquifers are capped by a solid rock layer with low CO_2 permeability that would ensure the CO_2 stayed permanently sequestered. These aquifers are deep underground and contain salt water making them unsuitable for drinking water supply, and large volumes of reservoirs are available for CO_2 sequestration. Both EOR and CO_2 injection into unminable coal seams results in the additional recovery of valuable products (oil and natural gas) which can help offset the cost of CO_2 capture and sequestration, but the capacities of these reservoirs are limited. Table-1.1 shows the capacity of the three types of reservoirs worldwide and the percentage of the projected CO_2 emissions from 2000 to 2050 each type of reservoir could sequester (Davison et al. 2001).

Table 1.1: Capacities of Natural Reservoirs for CO_2 Sequestration (Davison et al. 2001)

	Global Capacity	
	10^9 mton CO_2	% of emission to 2050
Depleted oil and gas fields	920.00	45.00
Deep saline reservoirs	400.00-10,000.00	20.00-500.00
Unminable coal seams	>15.00	>1.00

1.4 Scope of this Present Work

One of the main human CO_2 emissions sources is flue gases (flue gas streams, coal-fired power plants, refineries, cement manufacturing plants, etc.,) which contribute to the increasing greenhouse effect. Carbon dioxide capture in postcombustion is currently the most advanced technology and can be applied to existing plants. In the case of diluted and low-pressure steams, absorption based on chemical reaction with aqueous alkanolamine solutions is the most attractive technology. One of the advantages of alkanolamines is that, structurally, they contain at least one hydroxyl group, which helps to reduce their vapor pressures but increases their solubilities in aqueous solution.

On the other hand, the amino group provides for the necessary alkalinity to absorb CO_2 (Kohl, 1997). The most common alkanolamines are used in this process are MEA, DEA, MDEA, DIPA and AMP. Among all known solvents, ethanolamine (MEA) is the benchmark molecule because of its properties toward CO_2 capture (high absorption capacity, fast kinetics, high water solubility, low price, etc.). But MEA is rapidly displaced by more efficient systems. However, for low concentrations of H_2S and CO_2 it is preferred. This is especially for low pressure and maximum removal of H_2S and CO_2. The advantages are the high alkalinity and easy recovery from contaminated solutions. On the other hand an irreversible product is formed with COS and CS_2, it is more corrosive, high heat of reaction with CO_2 and also a high vapour pressure (Kohl A. L. R., 1979).

DEA is used for the treatment of refinery gases with COS and CS_2. DEA is less reactive with COS and CS_2 than MEA and also a lower vapour pressure is needed. The disadvantages of DEA treatment are that vacuum distillary is necessary and therefore difficult. And when a high content of CO_2 is present, DEA isn't a good choice because of the forming corrosive degradation products (Kohl A. L. R., 1979).

MDEA is another alkanolamine which can be used for the removal of CO_2. The advantages given by Appl in 1980 are low energy requirement, high capacity and high stability, the disadvantage the low rate of reaction with CO_2. The rate of the reaction can be increased by using promoters, without diminishing the MDEA advantages. MDEA is most used and described by Kohl (Kohl A. L. R., 1979). However, a major disadvantages associated with chemical absorption is solvent degradation which is defined as the undesirable breakdown of amine to unwanted byproducts by reversible or irreversible side reaction due to the presence of CO_2 and O_2. Byproducts lead to a significant decrease in efficiency of the process (solvent losses, corrosion, foaming, fouling, and an increase in viscosity).

This undesirable breakdown reduces their CO_2 absorption capacity and introduces unwanted degradation products, thus forcing the solutions to be eventually discarded. An operational burden such as corrosion is also induced, as it has been periodically reported that the degradation products can lead to severe corrosion (Blake, 1967; Rooney P C B, 1997). So, development of new amines with higher chemical stability has become essential. More and more attention has been paid to diamines recently; they seem to be good alternative solvents because their second amine function has close properties to alcohols and increases CO_2 absorption capacity.

The rate of the reaction, high stability, high absorption and resistance to degradation can be increased by using promoters, without diminishing the amine (MEA, DEA, MDEA) advantages. To improve the CO_2 removal processes different promoters are used. In 1980 piperazine (PZ) was found as an effective promotor for alkanolamine processes (Lensen, 2004). Recently, Piperazine (PZ) has been shown to be an effective promoter in MEA, MDEA, and potassium carbonate due to its rapid formation of carbamates with CO_2. PZ is more effective than the conventional rate accelerators that have been used as activator in the activated MDEA technology of BASF (Appl et al., 1982). Aqueous solutions of blended monoethanolamine (MEA) and piperazine (PZ) have also demonstrated their promise as a cost-effective solvent for carbon dioxide (CO_2) capture from industrial flue gas streams due to their absorption performance and energy efficiency (Dang H. R., 2003). This is also mentioned that, concentrated, aqueous piperazine (PZ) has been investigated as a novel amine solvent for carbon dioxide (CO_2) absorption and the absorption rate with aqueous PZ is more than double that of 7 m MEA and volatility at 40°C ranges from 10 to 19 ppm. Thermal degradation is negligible in concentrated PZ solutions up to a temperature of 150°C, a significant advantage over MEA systems (Freeman et al., 2009).

PZ-activated aqueous MDEA and AMP solutions combine the relatively high rate of reaction of the former with CO_2 with the lower heat of reaction of the later with CO_2. From

these considerations, (MDEA-PZ) and (AMP-PZ) solutions appear to be attractive new blended solvents for acid gas removal. While absorption of CO_2 into MDEA and AMP has been studied extensively in the past, only few publications have dealt with absorption of CO_2 into the blends of PZ with MDEA or AMP (Bishnoi and Rochelle 2000, and 2002; Seo and Hong 2000; Sun 2005; Xu et al 1992, 1995, and 1998; Zhang et al., 2001). Closmann et al in 2009 investigated that aqueous MDEA/PZ is an alternative to aqueous monoethanolamine (MEA) and aqueous K^+/PZ for CO_2 capture from coal-fired flue gases. This is an attractive solvent because it has greater capacity and lower equivalent work for CO_2 removal than MEA. MDEA/PZ has been successfully used for years in the natural gas industry for removal of CO_2 and hydrogen sulfide (H_2S).

In the mid-ninteen eighties, in order to further improve absorption performance of MDEA solvent, blended alkanolamine solvents have been developed by adding another alkanolamine into MDEA. These blended solvents include MDEA–MEA, MDEA–DEA, MDEA–DIPA, MDEA–DGA, and MDEA–AMP, etc.(Pacheco et al., 2000; Mandal et al., 2001; Xia et al., 2003; Rinker, 1997). The blended solvents have the compatibility of advantages of single solvent in blended solvents (Aroonwilas and Veawab, 2004). For example, a blended solvent, which consists of a mixture of primary or secondary amine with MDEA, combines the higher CO_2 reaction rates of the primary or secondary amine with the higher CO_2 loading capacity of the MDEA. Thus, the blended solvent providing both higher CO_2 reaction rate and higher CO_2 equilibrium capacity may result in substantial lower solvent circulation rates compared to a single solvent. So the development of a new solvent for maximum CO_2 absorption can be considered as a great invention of sour gas sweetening process. A large number amount of experimental work (Dawodu and A. Meisen, 1996; Dawodu and Axel Meisen, 1994; Lawal and Idem, 2006; Davis, 2009; Sexton and Rochelle, 2010; Lawal et al., 2005a; Oh et al., 2003) has been done over the past few years to characterize new solvents with respect to different properties (solubility, absorption, capacity,

amine volatility, etc.). Amines and alkanolamines are among several solvents that have been investigated and current research is focus on designing a chemically stable, less corrosive solvent with fast reaction rates and low heats of absorption to minimize energy requirements for the regeneration of the solvent. Recently, most of the scientists have shown an increased interest in the use of mixed amine solvents in gas-treating processes. Blends comprising of primary, secondary, or tertiary amines have been suggested for the industrial gas sweetening processes (Abdi et al., 2005). Some new amine blends (TBEE, APM, DIPATBG, and TBE) have been focused upon as having no sufficient reports on degradation.

Alkanolamines degradation with CO_2 has been studied for a while: N methyldiethanolamine (MDEA) and diethanolamine (DEA) are commonly used in natural gas treatment and MEA is the benchmark solvent for post combustion application. Contrary to the degradation with CO_2, under actual plant operating condition was not studied very much: only Chakma and Meisen established the relative stability of MDEA with temperature. Many authors were interested in MEA degradation with CO_2 and identified main byproducts such as 2-oxazolidinone, N-(2-hydroxyethyl) imidazolidinone, and N-(2-hydroxyethyl)-ethylenediamine (Polderman, 1955; Scheiman, 1962; Strazisar et al., 2003) . DEA degradation was first studied by Kennard and Meisen (Kennard, 1980; Meisen, 1982; Kennard and Meisen, 1983; Kennard and Allelsen, 1985) followed by Hsu (Hsu, 1985) and Holub (Holub, 1998). Finally, MDEA degradation was also investigated and some reaction mechanisms were suggested by Chakma and Meisen (Chakma, 1997; Chakma, 1988) and Clark (Clark, 2004). These studies permitted to show similarities between MEA, DEA, and MDEA degradation: in fact, the main products are amines, oxazolidinones, and imidazolidinones. Specific information was found on the degradation of alkanolamines blends rather than single amine's solution during sour gas absorption and stripping system but in the sweetening process amine blends are still using widely.

Degradation of MDEA/PZ blends was conducted by several researchers but it is not fully understand because so many degradation products were unidentified and unknown. On the contrary, DEA/PZ solvent blend have not yet been described in the literature, and to the best of our knowledge, this work is the first degradation study will be conducted in this project work. In order to have a better understanding of degradation phenomenon which has not yet been studied will approach was based on a stability comparison between activated and inactivated amine solvent in the presence of CO_2.

In this work, carbon dioxide induced degradation of activated DEA and MDEA will be studied. The liquid phase reaction samples will be characterized by using GC-MS, IC and HPLC (UV) in this investigation. The objectives to be achieved are ststed below.

1.5 Objectives of this Research

- To identify CO_2 induced degradation products of conventional DEA, MDEA and PZ.
- To identify CO_2 induced degradation products of activated DEA and MDEA (DEA/PZ and MDEA/PZ).
- To investigate the effect of amine concentration on the degradation process.
- A comparative study of degradation stsbility of two activated amine systems DEA/PZ and MDEA/PZ.

CHAPTER 02

LITERATURE REVIEW

CHAPTER 02: LITERATURE REVIEW

This chapter includes all relevant information pertaining to the all types of degradation of amines induced by sour gases like CO_2 and H_2S. Information of background of degradation, degradation chemistry, degradation mechanism and possible products is discussed. The experimental work of researchers who have studied amine degradation induced by CO_2 is presented and its relevance is placed in the scope of this work. In this chapter also focused amine degradation research gap closely related with this project.

2.1 What is Degradation and Degradation Products?

Degradation is an irreversible chemical transformation of alkanolamines into undesirable compounds resulting in its diminished ability to absorb acid gases. Degradation is undesirable and leads to substantial amine loss, impaired process efficiency and throughput and equipment fouling and corrosion (Lepaumier, H. D. et al., 2009a)**.** In another way **"**Degradation products are contaminants in solution that are derived from the breakdown of the base amine molecule and often caused reversibly and irreversibly to form totally different chemical species". Examples of degradation products are ethylenediamine derivatives (THEED) in the case of (DEA), which can form when CO_2, COS or O_2 are in an amine system.

$HO\text{-}C_2H_4NH_2 + HCl \longrightarrow HO\text{-}C_2H_4NH_3^+Cl^-$ ---------- 2.1
DEA HSS

$HO\text{-}C_2H_4NH_2 + H_2S \longrightarrow HO\text{-}C_2H_4NH_3^+HS^-$ ---------- 2.2
DEA HSS

$R\text{-}NH_2 + O_2 \longrightarrow C_nH_{2n+1}$-COOH / Imidazolidone ---------- 2.3

$MEA + CO_2 \longrightarrow$ OZD, HEI, HEED ---------- 2.4

MEA + COS ⟶ DEA Urea ---------- 2.5

$DEA + CO_2 \longrightarrow$ HEOD, BHEEP, THEED ---------- 2.6

DEA + COS ⟶ MEA, HEI, BHEED ---------- 2.7

$MDEA + CO_2 \longrightarrow$ EG, HMP, DEA, TEA, BHEP ---------- 2.8

$DGA + CO_2 \longrightarrow$ BHEEU ---------- 2.9

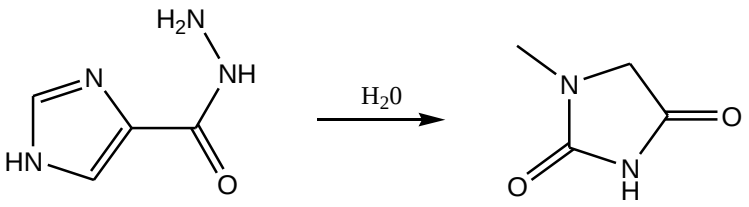
DGA + COS ⟶ BHEETU ---------- 2.10

$DIPA + CO_2 \longrightarrow$ HMPO ---------- 2.11

Reactions 2.1 to 2.11 represent the different degradation products induced by acid gases. Significant numbers of articles have been published in the field of degradation in the last three decades (Lepaumier et al., 2009c; Lepaumier et al., 2010,; Closmann et al., 2009). The prevention of amine loss, amine degradation is one of the conditions for successful plant operation and also the key to economic benefits.

2.2 Major causes of amine and alkanolamine degradation

Amines and alkanolamines can be degraded in many ways. During the absorption process amines and alkanolamine are used for removing acidic gases CO, CS_2, CO_2, COS and H_2S. Water is used as solvent for making amine solution, this makeup water causes the degradation of amine. It has been proved that water induced degradation products are also reactive to cause miscellaneous effect on plant equipments. An example of water induced degradation of amine given by the following chemical reaction [2.12 & 2.13], illustrated by Uyanga (2007).

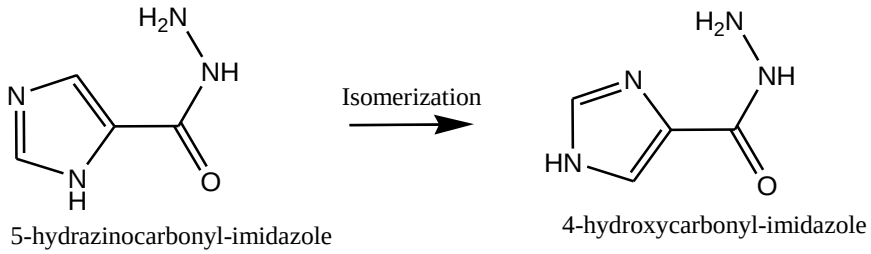


4-hydroxycarbonyl-imidazole 1-methyl-2, 4-imidazolidinedione

$$+ \quad 2NH^{+} \qquad [2.12]$$

$$2NH^{+} \xrightarrow{2H_2O} 2NH_3 + O_2 \qquad [2.13]$$

Carbon steel contains chromium, nickel, copper, vanadium and iron, which catalyze amine degradation process. These components also have various effects on amine degradation that are explained by Freeman (Freeman et al., 2010; Goff and Rochelle, 2006; Sexton and Rochelle, 2009b, a). Isomerization reaction takes place in the degradation of MEA sweetening process according to reaction [2.14] (Strazisar et al., 2003; Uyanga, 2007).

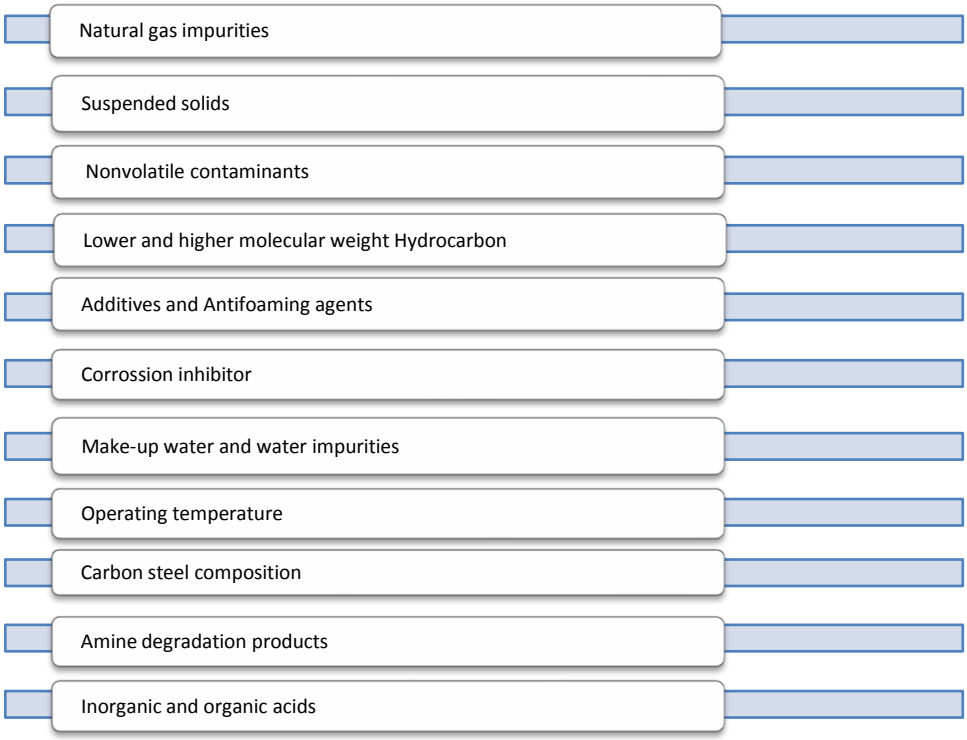


5-hydrazinocarbonyl-imidazole

4-hydroxycarbonyl-imidazole

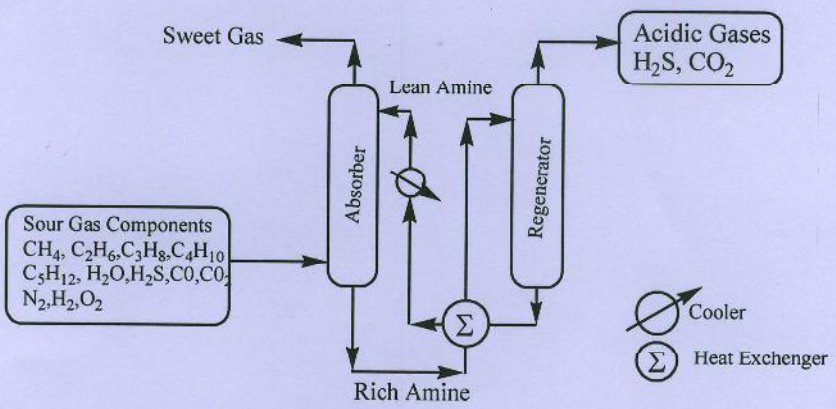
[2.14]

Several researcher carried out work on amine degradation reaction i.e. photo degradation (Klare et al., 2000; Klare et al., 1999; Chu et al., 2009; Mirkhani et al., 2009), oxidative degradation (Sexton and Rochelle, 2009b, a; Lepaumier et al., 2010,; Chi, 2000; Goff, 2005; Chi and Rochelle, 2010; Goff and Rochelle, 2010; Sexton and Rochelle, 2010; Lawal et al., 2005a), thermal degradation (Freeman et al., 2010; Davis and Gary Rochelle, 2009; Closmann et al., 2009; Freeman et al., 2009; Lepaumier et al., 2010,; Davis, 2009) and catalytic degradation (Freeman et al., 2010; Goff and Rochelle, 2006; Chi and Rochelle, 2010). Recently P. L. Carretty's and his co-workers in 2011 explained several reaction mechanisms, for e.g. Hoffmann reaction, ring opening reaction, elimination reaction, ring closure reaction, methylation, demethylation and polymerization reaction (Lepaumier et al., 2009a; Lepaumier et al., 2010,; Lepaumier et al., 2009c, b). Degradation reaction, that are induced by degradation products and their subsequent reaction by products (Dawodu and Meisen, 1996; Dawodu and Axel Meisen, 1994). Anti foaming agent, additives, corrosion inhibitor, particulates also cause degradation. Sakinul et al., (2011) have reviewed the previous work done on amine degradation products and come-up with the major cause of amine degradation as illustrated in the following diagram.



2.2.1 Degradation of alkanolamine induced by sour gas components

The main components of raw natural gas are methane, ethane, propane and butane which contain some acidic oxides. The acidic oxides are CO_2, H_2S and CO which can easily form different acids or acid substituted compounds shown in Figure 2.1. H_2S is also one of the more corrosive acids of contaminants; it can easily produce H_2SO_4 while undergoing hydrolysis reaction and finally interacts with amine and alkanolamines solvent. Similar reaction can be caused in the case of HNO_3 and contaminated amine solution by the formation of nitrate, nitrite and HSS salts. It is based on the reaction between weak acid (H_2S and/or CO_2) and weak base (alkanolamines) to give a water soluble amine acid gas salt. An amine based natural gas sweetening plant was configured with absorber and regenerator. The temperature range is 40-60˚C and 100-120˚C at the absorber and the stripper respectively. The sweet gas obtained from the absorber alternatively exhausts sour gas components at the stripper.



Amines/Alkanolamines + Sour Gas ⟶ Sweet Gas

$$\left[\begin{array}{l}\text{Natural Gas Components:}\\ CH_4,\ C_2H_6,\ C_3H_8,\ C_4H_{10},\ CO\\ C_5H_{12},\ CO_2,\ N_2,\ H_2,\ H_2S,\ O_2,\\ H_2O\end{array}\right] + \left[\begin{array}{c}\text{Absorber Chemicals:}\\ \text{Amines/Alkanolamines, Water}\end{array}\right] \underset{\Delta}{\rightleftharpoons} \text{Sweet Gas + DGP}$$

DGP= Degradation Products; Δ= Absorber/ Stripper Temperature

Fig.2.1: Formation of DGPs during sour gas sweetening process

Alkanolamine solvents MEA, DEA, MDEA, TEA, DGA, DIPA, AMP and PZ are used as absorbents for sweetening natural gas and for prolong use of this solvent that is transferred to the stripper for regeneration. Absorption and desorption are the common processes in these two units occurring continuously during the circulation of amine solvent. Hetherio, during sweetening process the amines simultaneously react with sour gas components and degrade. Sour gas also contains hydrocarbons that are slightly soluble in water which accelerates degradation product formation during sweetening process.

2.3 Chemistry of Degradation

The basic chemistry of degradation of alkanolamine is explained in the open literature (Wenten, 2010). Reactions 2.15 to 2.19 shows that amines occur due to the protonation and carbamate formation reaction brought about by the hydrolysis of water and acids.

$$H_2O \longrightarrow H^+ + OH^- \quad \text{2.15}$$
$$H_2S \longrightarrow H^+ + HS^- \quad \text{2.16}$$
$$CO_2 + H_2O \longrightarrow HCO_3^- + H^+ \quad \text{2.17}$$
$$RNH_2 + H^+ \longrightarrow RNH_3^+ \quad \text{2.18}$$
$$RNH_2 + CO_2 \longrightarrow RNHCOO^- + H^+ \quad \text{2.19}$$

The same reactions are also reported in the literature (Dawodu and Meisen, 1996; Choy and Meisen, 1980; Dawodu and Axel Meisen, 1994) for DEA degradation. Hydrogen sulfide emitts hydrogen ion (Eq. 2.20) in water and carbon dioxide as well as carbonyl sulfide and produces COS and H_2S respectively (Eq. 2.21). This reaction causes additional reactions with DEA molecule.

$$H_2S \rightleftharpoons H^+ + HS^- \quad \text{2.20}$$
$$CS_2 + H_2O \rightleftharpoons COS + H_2O \quad \text{2.21}$$
$$COS + H_2O \rightleftharpoons CO_2 + H_2S \quad \text{2.22}$$
$$H_2O + CO_2 \rightleftharpoons H^+ + HCO^-_3 \quad \text{2.23}$$

DEA reacts with CS_2 and successively produces DEA thiocarbamate salt (Eq. 2.24 & 2.25). On the other hand DEA produces carbamate with CO_2 (Eq. 2.27) then DEA carbamate reacts with MEA and DEA to form BHEED and THEED respectively, which further forms BHEI and BHEP. HEOD is a DGP of DEA which forms DEA carbamate. Protonated DEA reacts with CO_2 and converts into MEA, ethanol and water. Ethanol can easily degrade to aldehyde and then to an acid which forms various acetate and ester compounds in amine system. Reactions 2.24 to 2.34 give an insight into the reaction pathways.

$$DEA + CS_2 \rightleftharpoons \text{DEA dithiocarbamate} \quad (2.24)$$

$$\text{DEA dithiocarbamate} + DEA \rightarrow \text{DEA dithiocarbamate salt} \quad (2.25)$$

$$DEA + H^+ \rightleftharpoons DEAH^+ \quad (2.26)$$

$$DEA + CO_2 \rightleftharpoons DEACOO^-H^+ \quad (2.27)$$

$$DEAH^+ + CO_2 \rightleftharpoons MEA + C_2H_4OH + CO_2 \quad (2.28)$$

$$DEACOO^-H^+ + MEA \rightarrow BHEED + CO_2 + H_2O \quad (2.29)$$

$$DEACOO^-H^+ + DEA \rightarrow THEED + CO_2 + H_2O \quad (2.30)$$

$$THEED + CO_2 \rightarrow BHEP + CO_2 + H_2O \quad (2.31)$$

$$DEACOO^-H^+ \rightleftharpoons HEOD + H_2O \quad (2.32)$$

$$MEACOO^-H^+ + MEA \rightarrow HEI + H_2O \quad (2.33)$$

$$BHEED + CO_2 \rightarrow BHEI + H_2O \quad (2.34)$$

2.4 Effect of Degradation Products on Process Parameters

It is believed that degradation products cause major problems to process plant operation. Foaming induced by degradation products reported by by several researchers (Thitakamol et al., 2009; Thitakamol and Veawab, 2008; Goff and Rochelle, 2006). Corrosion problems due to degradation products were also reported by many authors (Dawodu and A. Meisen, 1996; Franco et al., 2009; Bedella, 2009; Eide-Haugmo et al., 2009). Bedella and his co-workers reported that several problems which occurred due to irreversible degradation reaction which are as follows (Bedella, 2009).

1. Reduction solution capacity and plant performance
2. Foaming effect of degradation products
3. Capital/Material of Construction Issues
4. Corrosion effect of degradation products
5. Environmental effect of degradation products.
6. Fouling effect of degradation products

2.5 Overview of the Historical Background of Degradation Study

Degradation study of alkanolamines (MEA, DEA and MDEA) was carried out by several authors in particularly MEA stuied by (Strazisar et al., 2003; Lepaumier et al., 2009a; Chi and Rochelle, 2002; Goff and Rochelle, 2004; Goff and Rochelle, 2006; Davis and Gary Rochelle, 2009; Klare et al., 2000; Franco et al., 2009; Shahi et al., 1994; Choy and Meisen, 1980; Dawodu and Meisen, 1991; Supap et al., 2006; Lepaumier et al., 2009c; Sexton and Rochelle, 2009a, b; Ayanduntan et al., 2006; Davis, 2009; Goff and Rochelle, 2010; Strazisar et al., 2010), MDEA (Lepaumier et al., 2009a; Blauwhoff et al., 1984; Closmann et al., 2009; Klare et al., 2000; Shahi et al., 1994; Lepaumier et al., 2009c) and DEA (Lepaumier et al., 2009a; Blauwhoff et al., 1984; Klare et al., 2000; Dawodu and Meisen, 1996; Shahi et al., 1994; Choy and Meisen, 1980; Dawodu and Meisen, 1991, 1992; Kennard M. and Axel Meisen, 1983; Lepaumier et al., 2009c, b) in the presence of H_2S, COS, CO_2 and/or O_2 were published in the last three decades. Dawodu and Meisen (1991) studied the thermal degradation of COS loaded DEA using GC and GC/MS techniques and they identified up to twenty degradation products. It was also found that the resistance to oxidative degradation follows the order: MDEA/PZ> MDEA>PZ and DGP were found in HSS, glycolate and formate (Closmann et al., 2009). Recently it was noted that PZ solutions were 3–5 times more resistant to oxidation than MEA (Stephanie et al., 2010; Freeman et al., 2010). The degradation of polyamines (TMPDA, TMBDA, PMDETA, PMDPTA, TMEDA) studied by (Lepaumier et al., 2010,) the author identified four main DGPs for each polyamine. The author also illustrated that tertiary amines were more stable primary and secondary amines. However, it is not always true; four tertiary polyamines DMP, TMEDA, TMPDA, and PMDPTA were shown to be more stable than MEA while two tertiary polyamines (TMBDA and PMDETA) were much less stable than MEA. Freeman investigated thermal degradation of PZ and showed that it is negligible in concentrated PZ solutions and up to a temperature of 150°C and had a significant advantage over MEA systems (Freeman et al.,

2009). Oxidative degradation of concentrated PZ solutions is appreciable in the presence of copper (4 mM), but negligible in the presence of chromium (0.6 mM), nickel (0.25 mM), iron (0.25 mM), and vanadium (0.1 mM). Degraded DEA solutions usually contain hydroxyethyl oxazolidone (HEOD) bis (hydroxyethy) piperazine (BHEP), and tris-(hydroxyethyl) ethtlendiamine (THEED), together with low concentrations of various higher boiling compounds (Dawodu and Meisen, 1996, 1993; Shahi et al., 1994; Choy and Meisen, 1980; Dawodu and Meisen, 1991; Dawodu and Axel Meisen, 1994). The degraded solution of MDEA or MDEA/PZ contains EG, DEA, TEA, DMAE, HMP, BHEP, MP and DMP (Lepaumier et al., 2009a; Lepaumier et al., 2009c, b; Oh et al., 2003; Amiri et al., 2007; Carlson et al., 2001; Haws and Jenkins, 2000). Literature cited sufficient information on MEA degradation products including volatile and solid substances. It contains more than 15 different degradation products identified by many researchers (Strazisar et al., 2003; Supap et al., 2006; Lepaumier et al., 2009c, b; Sexton and Rochelle, 2009b; Davis, 2009; Sexton and Rochelle, 2010; Strazisar et al., 2010; Haws, 2010). Haws noted that the degraded solution of DGA contains BHEEU and BHEETU, DIPA contains HMPO (Haws, 2010). In addition to these impurities, resulting from acid gas induced amine degradation, industrial amine solutions frequently contain other contaminants such as suspended solids, dissolved hydrocarbons, sodium and chloride ions, iron sulfide, foam suppressants, corrosion inhibitors and heat stable salts. The accumulation of contaminants in amine solutions creates major operational problems including degradation (Lepaumier et al., 2009a), foaming (Thitakamol et al., 2009; Pauley and Reza Hashemi, 1998; Amiri et al., 2007), fouling (Axel Meisen and Abdi, 2010), corrosion (Dawodu and A. Meisen, 1996), a reduction in active amine content also causes an increase in solution viscosity. The chemical and physical nature of the contaminants makes the development of purification schemes inherently difficult.

2.6 Degradation of Monoethanolamines (MEA) and its Blends

Monoethanolamine (MEA) is used extensively to remove CO_2 from flue gas, MEA degrades in the presence of O_2 and CO_2, resulting in extensive amine loss and equipment corrosion as well as generating environmental impacts. In power plant flue gas stream, that contains 5-10% O_2, 10% CO_2; three types of degradation can occur. Carbamate polymerization requires high temperatures and carbon dioxide (Goff, 2005). This reaction produces high molecular weight degradation products and is expected to occur at the higher temperature region of the stripper. Effectively to prevent MEA degradation, a degradation prevention strategy needs to be formulated, and this requires knowledge of the degradation products, stoichiometry, mechanism, and kinetics of the degradation process as a function of the various operating variables (Bello, 2006). Among all the alkanolamines MEA is more reactive also degrade easily compared to other amines. Literature cited more information on oxidative, thermal and photo degradation for MEA Table-2.1 presents previous work done on MEA degradation.

Table 2.1**:** Degradation report of monoethanolamine (MEA) [O=Oxidative, T=Thermal, D=Degradation, P=Photo]

ID No.	Author and Year	Major Study	Amine Solvent	Reaction Gases
[1]	(Strazisar et al., 2003)	O.D	MEA	CO_2
[3]	(Lepaumier et al., 2009a)	O.D	MEA with 17 different amines	CO_2, O_2
[4]	(Chi and Rochelle, 2002)	O.D	MEA	CO_2, O_2
[5]	(Bello, 2006)	Kinetics of O.D	MEA	CO_2, O_2
[6]	(Goff and Rochelle, 2004)	O.D	MEA	CO_2, O_2
[7]	(Goff and Rochelle, 2006)	O.D	MEA	CO_2
[8]	(Thitakamol et al., 2009)	Foaming nature	MEA	CO_2
[9]	P.M.M.Blauwhoff	Reaction of amines	MEA,DEA,MDEA,TEA,DIPA and so on	CO_2
[11]	G.T. Rochelle et. al	T.D	MEA	CO_2
[13]	(Klare et al., 2000)	P.D	MEA, DEA, MDEA and so on	TiO_2, TiO_2/Pt
[15]	(Franco et al., 2009)	O.D	MEA	CO_2
[23]	(Shahi et al., 1994)	Advantages of GC over various metd.	MEA; MEA+MDEA; DEA; AMP; MDEA	CO_2, H_2S
[27]	(Supap et al., 2006)	O.D	MEA	CO_2, O_2
[30]	(Lepaumier et al., 2009c)	O.D	MEA with 12 amines	CO_2
[31]	(Lepaumier et al., 2009b)	D	MEA with 12 amines	CO_2
[33]	(Sexton and Rochelle, 2009b)	O.D	MEA	CO_2, O_2
[34]	(Sexton and Rochelle, 2009a)	O.D	MEA	CO_2, O_2
[38]	(Lawal and Idem, 2006)	Kinetics of O.D	MEA+MDEA	CO_2, O_2
[39]	(Davis, 2009)	T.D	MEA	CO_2
[46]	(Chi and Rochelle, 2010)	O.D	MEA	CO_2
[47]	(Goff and Rochelle, 2004)	O.D	MEA	CO_2, O_2
[48]	(Sexton and Rochelle, 2010)	O.D	MEA+PZ	CO_2, O_2
[49]	(Lawal et al., 2005a)	Reaction Mechanism of D	MEA; MEA+MDEA	CO_2, O_2
[51]	(Strazisar et al., 2010)	D	MEA	CO_2

2.6.1 Degradation products of MEA and its Blends

Degraded solutions of MEA were analyzed by GC, GC-MS, IC, NMR, FT-IR and HPLC and identified more than fifteen degradation products. Generally IC was conducted to detect lower molecular weight compounds e.g. salt of inorganic acids and organic acids. GC, GC-MS and HPLC analysis detected higher molecular weight compounds. Rate of degradation and volatile DGP were identified by FTIR. The miscellaneous degradation products and used methodologies are given in Table- 2.2, 2.3 and 2.4.

Among these various methods IC basically used to detect ionic degradation products. On the otherhand gaseous products are ammonia is identified by FTIR. The molar mass compounds and higher molar mass compounds are detectd by HPLC and GC-MS methods but sometimes polymerics compounds are also found to detect by these methods too. Identification of degradation products by chromatographic methods, the column, solvent and overall method selections are most importants factors. Table 2.2 is an insight of all important factors of degradation studies of MEA during sour gas sweetening process. In the open literature most of the articles emphasised on the detection DGPs rather than the effect.

Table 2.2: Degradation products of monoethanolamine (MEA)

ID No.	Methodology	Column	Length × ID × Thickness	Findings
[1]	GC-MS;GC-FTIR;GC-AED	DB-1701	60m × 0.32mm × 0.25-µm	19 DGPs are identified
		Nukol	60m × 0.25mm × 0.25-µm	
[3]	GC; GC-MS; FT-ICR/MS; NMR	Not available	Not available	17 DGPs are identified **(Table: 2.3)** and ionic DGPs are acetic, glycolic and oxalic acids as well as nitrate, nitrite are also identified with possible reaction mechanism of degradation
[4]	NH_3 evaluation	N/A	N/A	Effect of EDTA, Bicine, CO_2loading and Iron ion were investigated
[5]	HPLC	Shodex IC YK-421 Shodex IC YK-G	Not avaiable	Kinetics of oxidative degradation of MEA induced by CO_2
[6]	Degradation rates were quantified by measuring the rate of NH_3 evolution from the amine solutions using FT-IR analysis. Results show that degradation rates are controlled by the rate of physical absorption of O_2 and NH_3 evolution rates ranged from 0.2 to 8.0 mM/h.			
[7]	This study examines the effect of a number of additives on the oxidative degradation of monoethanolamine (MEA) in the presence of dissolved Cu.			
[8]	ASTM D892	Foaming behavior of MEA and its degradation was investigated. Foam height increases with gas flow rate, solution volume, CO2 loading, MEA concentration, but decreases with solution temperature. Most degradation products and corrosion inhibitors in aqueous MEA solutions enhance foaminess coefficient, except for sulfuric acid. Physical properties, namely surface tension, density and viscosity of solution, play a significant role in foaming tendency through foam formation and foam stability.		
[9]	Rate of reaction between CO_2 and MEA, DEA, MDEA, TEA, DIPA were conducted here. The experimental technique was similar to that used by Laddha and Daockwerts [72].			
[11]	IC, HPLC, MS	Not available	Not available	HEIA, HEEDA and MEA-Urea
[13]	TOC, IC	Not available	Not available	Ammonium, Nitrate, nitrite
[15]				Effect of amine degradation
[23]	GC	Tenax GC	6 ft × 1/8 in and mesh 80-100	GC is better than $BaCl_2$ and volumetric method
[27]	GC-MS	HP-35MS; HP-5MS; HP-Innowax	30m × 0.25mm × 0.25-µm (Same dimension for all)	Identified DGPs are shown in **Table 2.4** Major DGP were identified=24 Additional Products are Found=8 Previously Reported Degradation Products=3
	HPLC-RID	Nucleosil 100-5 SA	250 m × 4.6 mm (Packed)	
		Shodex YK-421	125 m × 4.6mm (Packed)	
	CE-DAD	Bare fused silica cap.column	805mm-length × 0.25-µm -id	

Table 2.2: Continued

ID No.	Methodology	Column	Length × ID × Thickness	Findings
[30]	GC	CARBOWAX-Amines	15m × 530-ųm ×1.0-µm	4 main DGPs are identified
		CPSIL8-CB-Amines	25m × 320-ųm ×1.2-µm	
	GC-MS/ EI	CPSIL8-CB-Amines	30m × 250-ųm × 1.2-µm	
	GC-MS/CI	HP5-MS	30m × 225-ųm × 0.25-µm	
	NMR	N/A	N/A	
	IC	AS-15	4mm ID × 250 mm length	Oxalate, glycolate, formate, acetate, nitrate, nitrite
[31]	GC	CARBOWAX-Amines	15m × 530-ųm ×1.0-µm	4 main DGPs are identified
		CPSIL8-CB-Amines	25m × 320-ųm ×1.2-µm	
	GC-MS/ EI	CPSIL8-CB-Amines	30m × 250-ųm × 1.2-µm	
	GC-MS/ CI	HP5-MS	30m × 225-ųm × 0.25-µm	
	NMR	N/A	N/A	
	IC	AS-15	4mm ID × 250 mm length	Oxalate, glycolate, formate, acetate, nitrate, nitrite
[33]	HPLC	Not available	Not available	HEF, HEI
	IC	Not available	Not available	Oxamide, formate, formamide, oxalate, nitrite
[34]	HPLC	Not available	Not available	HEI, HEF
	IC	(AS-15+AG-15) CS-17	Not available	Oxamide, formate, formamide
	FT-IR	Not available	Not available	NH_3, CO, NO, H-CHO, CH_3-CHO, N_2O, C_2H_4
[38]	HPLC	Shodex IC YK-421	125mm × 4.6 mm	Degradation of MEA or MEA-MDEA blends is zero at higher loading of CO_2
		Shodex IC YK-G	10 mm × 10 mm	
[39]	HPLC	C_{18}	150 mm × 4.6 mm	OZD, HEIA, HEEDA, MEA-Urea, MEA-Trimer, Cyclic urea of HEEDA, MEA/HEEDA Urea, MEA-Quatramer, Cyclic urea of MEA-Quatramer.
	IC-MS and IC	CS 17	50 mm × 4 mm	
		CG 17	50 mm × 4 mm	
	NMR	N/A	N/A	
[46]	The rate of oxidative degradation of MEA by evaluating of NH_3 with FT-IR were studied and the effect of metal ions (Iron, Cupper) and EDTA conducted			
[47]	This study examines the rate of oxidative degradation of MEA by evaluation of NH_3 with FT-IR analysis			
[48]	IC	AS 15, CS 17	Not available	Oxalate, glycolate, formate, acetate, nitrate, nitrite, EDA
[49]	This papers mainly studied the degradation reaction pathways of MEA and MEA –MDEA blends induced by CO_2 and O_2			
[51]	GC-MS	DB-1701	60m × 0.32mm × 0.25-µm	DGP No: 2-7,12-19 [Table 2.3] and $C_4H_8N_2O_3$, $C_6H_{11}NO_3$
		Nukol	60m × 0.25mm × 0.25-µm	
	GC-FTIR			

Table 2.3: Degradation products of MEA+ CO_2+ H_2O system [ID No. 3]

DGP No	Compound name and formula	DGP No	Compound name and formula
1	N-formylethanolamine ($C_3H_7NO_2$)	11	2-hydroxyethylamino-N-hydroxyethylacetamide ($C_6H_{14}N_2O_3$)
2	N-acetylethanolamine ($C_4H_9NO_2$)	12	Ammonia (NH_3)
3	2-oxazolidone ($C_3H_5NO_2$)	13	Acetic acid ($C_2H_4O_2$)
4	N-(hydroxyethyl)-succinimide ($C_6H_9NO_3$)	14	Propionic acid ($C_3H_6O_2$)
5	N-(2-hydroxyethyl)-lanthamide ($C_5H_{11}NO_3$)	15	n-butyric acid ($C_4H_8O_2$)
6	1-hydroxyethyl-3-homopiperazine ($C_7H_{14}N_2O_2$)	16	Monoethanolamine (C_2H_7NO)
7	1-(2-hydroxyethyl)-2-imidazolidinone ($C_5H_{10}N_2O_2$)	17	2,6-dimethyl-4-pyridinamine ($C_7H_{10}N_2$)
8	1-hydroxyethyl-2-piperazinone ($C_6H_{12}N_2O_2$)	18	2-imidazolecarboxaldehyde ($C_4H_4N_2O$)
9	4-hydroxyethyl-2-piperizinone ($C_6H_{12}N_2O_2$)	19	1-methyl-2-imidazolecarboxaldehyde ($C_5H_6N_2O$)
10	3-hydroxyethylamino-N-hydroxy-ethylpropanamide ($C_7H_{16}N_2O_3$)		

Table 2.4: Degradation products of MEA/H_2O/O_2 and MEA/H_2O/CO_2/O_2 system [ID No. 27]

Major Identified DGPs	1-methylazetidine; D,L-homoserine lactone; Imidazole; N-(2-hydroxyethyl)acetamide; N-methyl formamide; 1,3-dioxane; 2-ethyl-1H-imidazole; 5-hydrazinocarbonyl-1H-imidazole; Uracil N-(2-hydroxyethyl)succinimide; 1-amino-4-methylpiperazine; 2-pyrolidinone; 1-methyl-4-imidazole-5-carboxylic acid; N-methylene ethanamine; 5-aminovaleric acid; D,L-aspartic acid; 2-[(2-aminoethyl)amino] ethanol; Ethylamine; 4,5dimethyloxazole; 18-crown-6; Ethylurea; N-glycylglycine dimethylhydrazone-2-propanone; 1-(2-hydroxyethyl)-2-imidazolidinone = 24
Additional DGPs	Ammonia; Formic acid; Acetic acid; Pyrimidine; Acetamide; 2-methylaminoethanol; Acetaldehyde; Ethanol=8
Previously Reported DGPs	Oxalic acid; Glycolic acid; Bicine =3

2.6.2 Degradation reaction of MEA and MEA blends

Carbon dioxide (CO_2) induced degradation reaction mechanism of MEA is illustrated by Fred Closmann (Oral presentation, 2009) which shown in the Figure 2.2. The mechanism is different from that of Lepaumier's studies (Lepaumier et al., 2009a; Lepaumier et al., 2009c, b) their results differ with respect to polymeric and oligomer degradation product. Oligomer is formed from O_2/CO_2 induced degradation of MEA (Lepaumier et al., 2009a; Lepaumier et al., 2009c, b). On the other hand F. Closmann is notted that these are polymeric degradation products formation (Closmann, 2009). Divergent views on the formation of either polymer or oligomer. The degradation pathways of MEA are explained in the literature (Strazisar et al., 2003; Goff and Rochelle, 2004; Lepaumier et al., 2009a; Lepaumier et al., 2009c, b; Abdi, 1997; Lawal et al., 2005a; Strazisar et al., 2010) for protonation reaction, polymerization reaction, isomerization reaction and miscellaneous routes. Oxidative and thermal degradation studies of MEA were conducted by G.T. Rochelle research group (Chi and Rochelle, 2002; Goff and Rochelle, 2004; Goff and Rochelle, 2006; Davis and Gary Rochelle, 2009; Sexton and Rochelle, 2009b, a; Goff and Rochelle, 2010), (Lepaumier et al., 2009a; Lepaumier et al., 2009c, b) and also many articles (Klare et al., 2000; Franco et al., 2009; Shahi et al., 1994; Supap et al., 2006; Abdi, 1997) they attributed the degradation was enhanced by corrosion inhibitor. Strazisar (Strazisar et al., 2003; Strazisar et al., 2010) conducted an experiment on reclaimer bottom solution of MEA solvent and found nineteen (19) degradation products. They explained that the same study was done in the laboratory scale but did not find all the degradation products. It is believed that MEA degradation reaction in plant operation is different from the laboratory condition, as some external degradation reaction occurred in the plant but not in the laboratory. They predicted a new route for alkanolamine degradation reaction mechanism of MEA degradation proposed by Uyanga (Uyanga, 2007) in case of a single solvent and/or blended with MDEA, on the other hand same degradation mechanism induced by O_2 was also discussed by Lawal (Lawal et al., 2005a).

The mechanisms are different from each other in case of single amine system. Careette and his co-workers conducted reaction mechanism of several ethanolamine and ethylenediamines including MEA, DEA, MDEA, AMP and DMAE (Lepaumier et al., 2009a; Lepaumier et al., 2009c, b). The reaction mechanism is not similar to Bello and Idem. Lepaumier et al. focused on four main degradation products through their mechanism, Bello and Idem focused on more than four different degradation products (Bello, 2006).

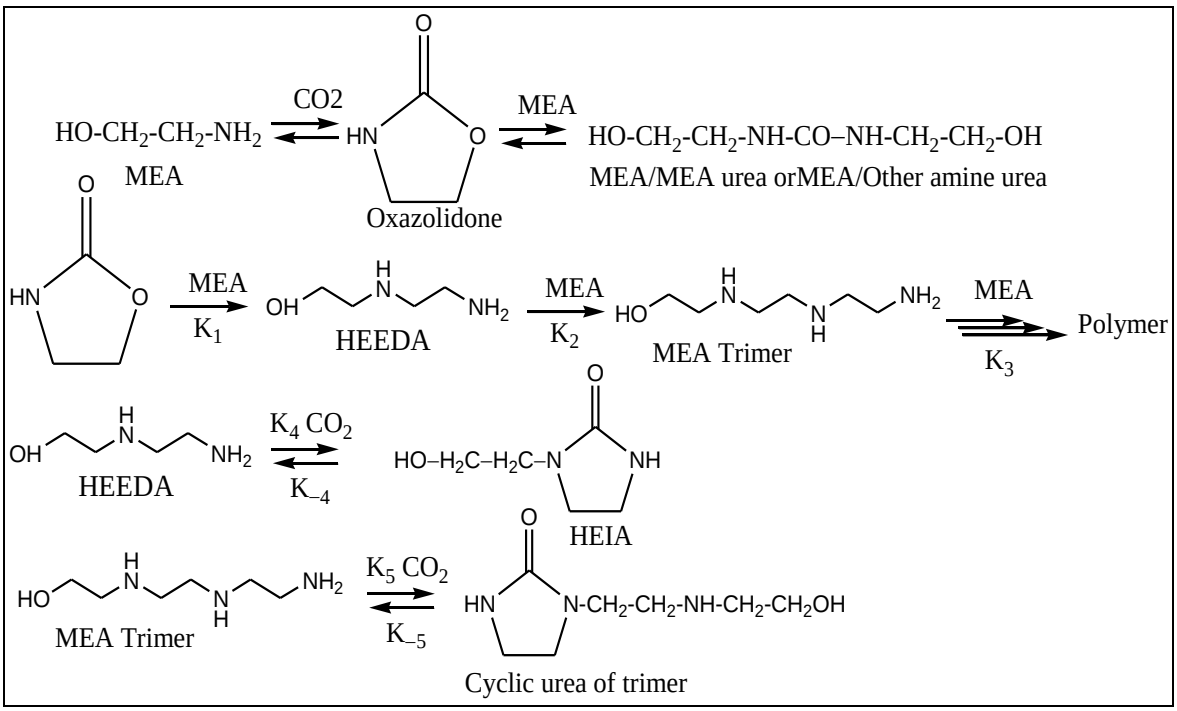


Figure 2.2: Degradation reaction mechanism of monoethanolamine (MEA) induced by carbon dioxide (CO_2).

2.7 Degradation of Diethanolamine (DEA) and its Blends

Aqueous diethanolamine (DEA) solutions are widely used in the oil and natural gas industries for the absorption of carbon dioxide and hydrogen sulfide from mixtures of light hydrocarbons. The amine solutions are subjected to regeneration by steam stripping before recycling to the absorber. Although the principal reactions governing absorption and desorption are certain, side reactions occur as well. Basically these side reactions are undesirable because they result in a loss of valuable amine and give rise to degradation products, some of which are highly corrosive. Table-2.5 reveals the degradation background of DEA.

Diethanolamine (DEA) is an important alkanolamine successfully used within the 25–35 wt% range in natural gas sweetening plant for sour gas absorption. Degradation study of DEA with CO_2 to form various byproducts has been demonstrated as early as 1956. Sufficient information on DEA degradation and its blends were reported in the literature (Lepaumier et al., 2009a; Blauwhoff et al., 1984; Klare et al., 2000; Dawodu and Meisen, 1996; Shahi et al., 1994; Choy and Meisen, 1980; Dawodu and Meisen, 1991, 1992; Kennard M. and Axel Meisen, 1983; Lepaumier et al., 2009c, b). DEA/MDEA and DEA/AMP also have an experience of sour gas absorption. The first blends MDEA/DEA have been used successfully in a wide variety of natural gas sweetening applications for 20 years. In 1956, Poldermann and Steele discovered the following reaction mechanisms (Section: 2.7.2, Figure 2.3 and Figure 2.4) during DEA/CO_2 degradation. The author also mentioned that the BHEP is a basic characteristics compound so it has no corrosion effect. Table-2.6 reveals literature information on DEA degradation.

Table 2.5: Degradation background of DEA [D=Degradation, C=Corrosion behavior]

Author's Name (Ref.)	Year	Reaction Gases	Solvent	Findings
Polderman and Steele	1956	CO_2	DEA	D+C
McNab and Treseder	1971	CO_2, CO_2/H_2S	DEA	D+C
Choy and Meisen	1977	CO_2	DEA	D+C
Kennerd and Meisen	1980	CO_2	DEA	D+C
Blanc, Grall and Demarais	1982	CO_2	DEA	D+C
Chakma and Meisen	1984	CO_2	DEA	D+C
Kim and sartori	1984	CO_2, H_2S, CO_2/H_2S	DEA	D+C
Kennard and Meisen	1985	CO_2	DEA	D+C
Hsu and Kim	1985	CO_2	DEA	D+C
Chakma and Meisen	1986	CO_2	DEA	D+C
Dawodu and Meisen	1996	CO_2	MDEA/DEA	D+C
Holub, Critchfield and Su	1998	CO_2	DEA, DEA/MDEA	D+C

N.B: D=Degradation; C=Corrosion

Table 2.6: Degradation report of DEA

ID No.	References	Major Study	Amine Solvent	Reaction Gases
[3]	(Lepaumier et al., 2009a)	O.D	DEA with 17 different amines	CO_2, O_2
[9]	(Blauwhoff et al., 1984)	Reaction of amines	DEA,MEA,MDEA,TEA,DIPA and so on	CO_2
[13]	(Klare et al., 2000)	P.D	DEA, MDEA, MEA and so on	TiO_2, TiO_2/Pt
[21]	(Dawodu and Meisen, 1996)	D	DEA	CS_2
[23]	(Shahi et al., 1994)	Advantages of GC over various metds.	DEA; MEA; MEA+MDEA; AMP; MDEA	CO_2, H_2S
[24]	(Choy and Meisen, 1980)	GC analysis	DEA	CO_2, H_2S
[25]	(Dawodu and Meisen, 1991)	GCMS analysis	DEA	COS
[26]	(Dawodu and Meisen, 1992)	Effect of variables	DEA	COS
[28]	(Kennard and Meisen, 1983)	D	DEA	CO_2, H_2S
[30]	(Lepaumier et al., 2009c)	O.D	DEA with 12 amines	CO_2
[31]	(Lepaumier et al., 2009b)	D	DEA with 12 amines	CO_2
[37]	(Dawodu and Axel Meisen, 1994)	M, K	DEA	COS
[40]	(Abdi, 1997)	Purification of partially degraded DEA solution by different methodology		
[44]	(Sexton, 2008)	O.D	DEA; DGA; MEA; PZ	CO_2, O_2
[53]	(Amiri et al., 2007)	Foaming	DEA; MDEA	O_2

O=Oxidative, T=Thermal, D=Degradation, P=Photo

2.7.1 Degradation products of DEA and DEA blends with methods

The absorption rate of DEA is comparatively lower than that of MEA. However, it has better stability over MEA and its blends. Degradation results of DEA were found mostly from studies conducted by the Meisen and Chakma research group. DEA degradation studies (Versteeg and Oyevaar, 1989; Lepaumier et al., 2009a; Blauwhoff et al., 1984; Klare et al., 2000; Dawodu and Meisen, 1996; Shahi et al., 1994; Choy and Meisen, 1980; Dawodu and Meisen, 1991, 1992; Kennard M. and Axel Meisen, 1983; Lepaumier et al., 2009c, b) critically reviewed and all its degradation products are reported in the Table-2.7 and 2.8. DEA is not reclaimable under regenerator conditions (Meisen and Abdi, 2010); it decomposes below its boiling point at atmospheric pressure. Vacuum reclaimers, however, have been successfully used to reclaim DEA solutions (Meisen et al, 1996). Since DEA is a secondary alkanolamine, it has a reduced affinity to reaction with H_2S and CO_2.

Table 2.7: Degradation products of DEA

ID No.	Methodology	Column	Length × ID × Thickness	Findings
[3]	GC; GC-MS; FT-ICR/MS; NMR	Not available	Not available	17 DGPs are identified **(Table: 2.3)** and ionic DGPs are acetic, glycolic and oxalic acids as well as nitrate, nitrite are also identified with possible reaction mechanism of degradation
[9]	Not reported	Not reported	Not reported	MEA reaction with CO_2, DEA, MDEA, TEA,DIPA and so on
[13]	TOC, IC	Not available	Not available	Ammonium, Nitrate, nitrite
[21]	GC; GC-MS and elementary method	Tenax TA (Packed column)	9 ft × 1/8 in ID and mesh 80-100	BHEED, BHEP, HEOD, BHEI, HEI, THEED, DEAC, MEAC, DEADTC, MEA, MDEA, Polymer products are showed in **Table 2.8.**
[23]	GC	Tenax GC (175-147 ųm) Packed column	6 ft × 1/8 in and mesh 80-100	GC is better than $BaCl_2$ and volumetric method
[24]	GC	OV-17-Chromosorb W HP. Packed with 80-100 mesh Chromesorb W HP coated with 8% OV-17.	The column was made of 316 stainless steel, 6 ft. x I/8 in. O.D, (1830 x 0.32 mm 0-D.)	HEI, HEOD, HEP,THEED, MDEA, OZD, AEEA and miscellaneous products.
[25]	GC-MS, Melting point determinations and Elemental and Infrared analyses were used.	Tenax GC (60-80 mesh) Packed column	9 ft × 1/8 in ID	MEA,HEP, BHEED, BHEP, HEOD, HEI, BHEI, THEED,Eethylaminoethanol,Ethyldiethanolamine, Hydroxyethylacetamide, Eethanethioic acid S-Hydroxyethylaminomethyl ester, Acetaldehyde, acetone, Butanone, Acetic acid, Ethanol, Diethyl disulphide, Dithiane and pyridines.
[26]	The study shows that, to minimize degradation and plant operating problems, the solution temperatures should be kept low (preferably under 120°C). The solutions should be filtered and COS hydrolysis should be maximized.			MEA, BHEED, BHEP, HEOD, HEI, BHEI, THEED and Insoluble products these 8 DGP highlighted in case of COS/DEA in this paper.
[28]	GC/FID	O.D. stainless-steel column (Packed with 60-80-mesh Tenax GC)	6 ft. x I/8 in. O.D (1830 x 0.32 mm 0.D.)	Apart from MEA, DEA, TEA 11 DGPs were identified eg. HEP, BHEED, BHEP, HEOD, HEI, BHEI, THEED, HEM, HEED, OZD, BHEEP and N,N,N,N-Tetra (hydroxyethyl)-ethylenediamine.

Table 2.7: Continued

[30]	GC	CARBOWAX-Amines	15m × 530-ųm ×1.0-µm	4 main DGPs are identified
		CPSIL8-CB-Amines	25m × 320-ųm ×1.2-µm	
	GC-MS/ EI	CPSIL8-CB-Amines	30m × 250-ųm × 1.2-µm	
	GC-MS/CI	HP5-MS	30m × 225-ųm × 0.25-µm	
	NMR	N/A	N/A	
	IC	AS-15	4mm ID × 250 mm length	DGPs: Oxalate, glycolate, formate, acetate, nitrate, nitrite
[31]	GC	CARBOWAX-Amines	15m × 530-ųm ×1.0-µm	4 main DGPs are identified
		CPSIL8-CB-Amines	25m × 320-ųm ×1.2-µm	
	GC-MS/ EI	CPSIL8-CB-Amines	30m × 250-ųm × 1.2-µm	
	GC-MS/ CI	HP5-MS	30m × 225-ųm × 0.25-µm	
	NMR	N/A	N/A	
	IC	AS-15	4mm ID × 250 mm length	Oxalate, glycolate, formate, acetate, nitrate, nitrite
[37]	GC-MS method is used in this detection but analytical column details are not reported		15 DGPs are identified i.e. MEA, EAE, DEA, EDEA, HEA, HEP, ETAHEAME, BHEED, BHEP, HEOD, HEI, THEED, BHEI, Acetone and Butanone. Mathmatical modeling and rate constant also conducted in case of DEA/COS degradation.	
[40]	This study reported information on the purification of partially degraded DEA solution by miscellaneous methods.			
[44]	AIC Dionex ICS- 3000	AS15	4mm × 250 mm	Acetate, Glycolate, Formate, nitrate, nitrite, and Oxalate
		AG15	4mm × 50 mm	
	CIC Dionex ICS- 3000	CS17	4mm × 250 mm	All metal ions
		CG17	4mm × 50 mm	
	HPLC/ELSD	T3 C18	Nonionic products HEI, HEF and DEA, a secondary ethanolamine, oxidized to form Nformyldiethanolamine, formate and other unknown HPLC products in the presence of Fe.	
	FTIR	NA	NA	Volatile products
	TOC	Not reported	Not reported	Total C atom
[53]	Results of investigations shows higher foaming tendency and stability in higher gas flow rate in case of DEA and MDEA blends. Amine degradation products may also affects the surface tension and increasing foaming behavior.			

Table 2.8: Degradation products of DEA induced by CS_2 [ID. No. 21]

No D.P	Abbreviation	Degradation Products of DEA	Molecular Formullah
1	MEA	Monoethanolamine	C_2H_7NO
2	AMP	Aminomethyl propanol	$C_4H_{11}NO$
3	DGA	Diglycolamine	$C_4H_{11}NO_2$
4	HEP	Hydroxyethyl piperazine	$C_6H_{14}N_2O$
5	BHEED	N,N'-Bis(hydroxyethyl)-ethylenediamine	$C_6H_{16}N_2O_2$
6	DIPA	Di-isopropanolamine	$C_6H_{15}NO_2$
7	DEA	Diethanolamine	$C_4H_{11}NO_2$
8	BHEP	N,N'-Bis(hydroxyethyl)-piperazine	$C_8H_{18}N_2O_2$
9	BHEED	N,N-Bis(hydroxyethyl)-ethylenediamine	$C_6H_{16}N_2O_2$
10	HEOD	Hydroxyethyl-oxazolidone	$C_5H_9NO_3$
11	HEI	Hydroxyethyl-imidazolidone	$C_6H_{11}NO_2$
12	THEED	N,N,N'-Tris(hydroxyethyl)-ethylenediamine	$C_8H_{20}N_2O_3$
13	BHEI	N,N'-Bis(hydroxyethyl)-imidazolidone	$C_7H_{14}N_2O_3$
14	DEAC	Diethanolamine carbamat	$C_5H_{12}NO_4$
15	MEAC	Monoethanolamine carbamat	$C_3H_8NO_3$
16	DEADTC	Diethanolamine dithiocarbamate	$C_5H_{11}NS_2$
17	DEADTCS	Diethanolamine dithiocarbamate salt	$C_9H_{22}N_2O_4S_2$
18	AEEA	Aminoethylethanolamine	$C_4H_{12}N_2O$

2.7.2 Mechanism of DEA Degradation

A model was developed by Kennard (1983) that explained the formation of the main degradation products. The following two reaction mechanism (Figures 2.3 and 2.4) of DEA induced by CO_2 shows the major reactions which are believed to be responsible for the degradation of DEA by CO_2 (Reaction scheme A and B). Certain reaction steps cannot be fully confirmed since they are based on the existence of DEA carbamate. Unfortunately, it was impossible to isolate and identify the carbamate, and certain aspects of the reaction mechanism therefore they remain conjectural (Dupart et al., 1999).

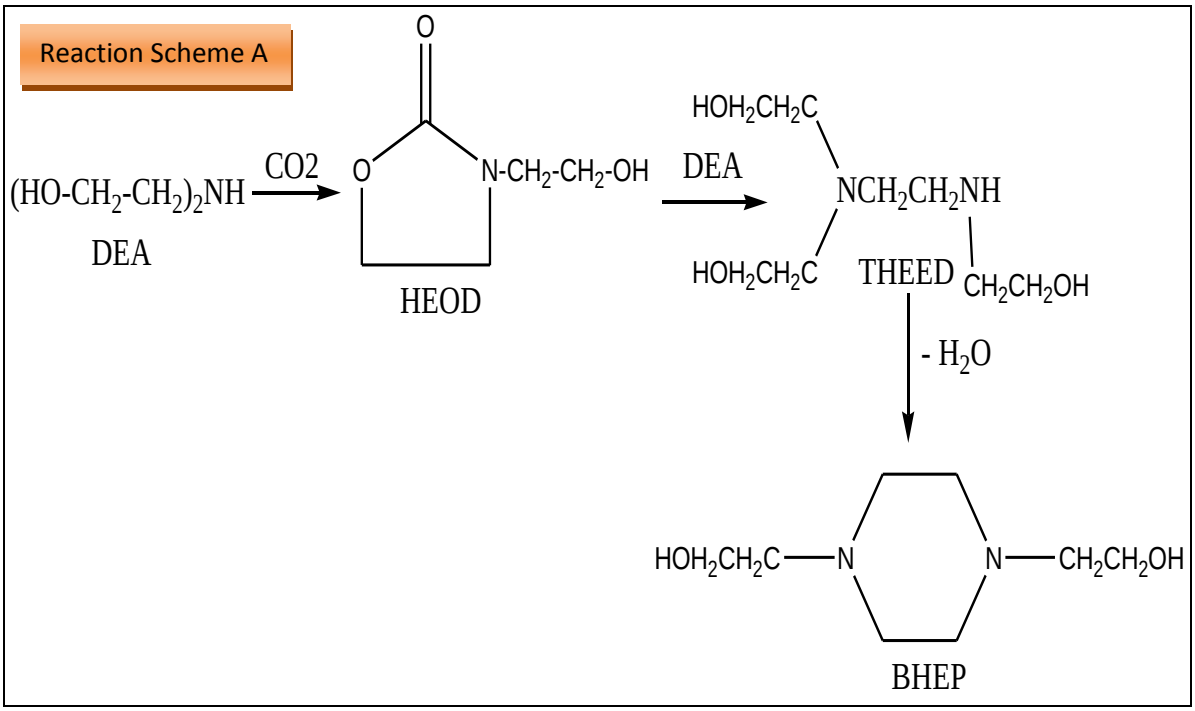


Figure 2.3: CO_2 induced degradation of DEA (Dupart et al., 1999).

In general, the DEA degrades via three routes: the fast "molecular route", the slower "ionic route", and the very slow "thermal route". The molecular route involves CO_2 reacting directly with DEA to produce the carbamate, whereas the ionic route produces the carbamate from the amine salt R_2NH^{2+}-HCO_3^-. The carbamate then degrades slowly to produce THEED, which in turn loses water to form BHEP. HEOD is a side product, produced by internal dehydration of the carbamate and it is believed that the formation of HEOD does not contribute to the overall degradation of DEA. CO_2 appears to catalyze the degradation of DEA to THEED and of THEED to BHEP via the formation of carbamate complexes [Figure 2.4, Reaction Scheme-B].

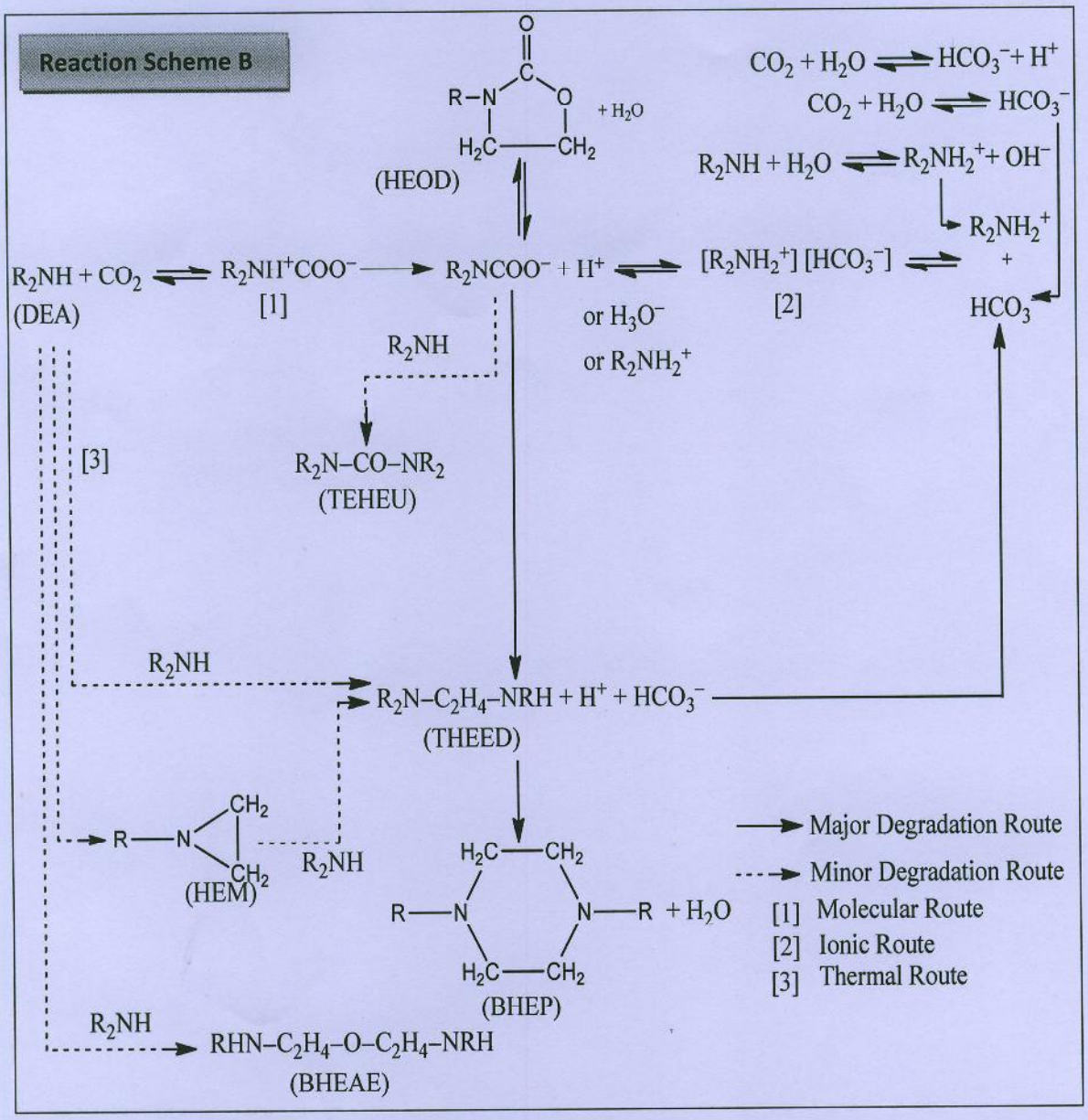


Figure 2.4: Possible route of DEA degradation reaction explained by (Kennard and Allelsen, 1985).

2.8 Degradation of Methyldiethanolamines (MDEA) and its Blends

MDEA is a tertiary amine and commonly used in the 20–50 wt% range which has a CO_2 loading capacity that approaches 1.0 mol/mol. Literature cited that, under proper experimental condition MDEA is more prone to oxidative degradation and when used in a mixture with MEA, and is preferentially degraded to protect MEA (Lawal et al., 2005b). The solvent blend methyldiethanolamine/piperazine (MDEA/PZ) has been investigated as an alternative to CO_2 capture from coal-fired power plants. MDEA/PZ offers an advantage over monoethanolamine (MEA) and MDEA alone because of its resistance to thermal and oxidative degradation at typical absorption/stripping conditions (Closmann et al., 2009). The degradation study of MDEA induced by CO_2/O_2, CO_2/H_2S and CO_2 were conducted by many researchers (Closmann et al., 2009; Klare et al., 2000; Shahi et al., 1994; Lepaumier et al., 2009c; Lawal et al., 2005b) and found that, solutions with lower amine concentration are typically employed in low-pressure, high-selectivity applications such as the selective removal of H_2S.

MDEA has several distinct advantages over primary and secondary amines, which include lower vapour pressure, lower heats of reaction, higher resistance to degradation, and lower corrosion rate. Most of these advantages have also been reported by Blanc et al (1982). Depending on the application, some of them have special significance; for example, due to its lower heat of reaction, MDEA can be employed. Table-2.9 illustrates previous research work done on MDEA degradation.

Table 2.9: Degradation reports of MDEA and MDEA-blends.

ID No.	Author and Year	Major Study	Solvent	Reaction gases
[3]	(Lepaumier et al., 2009a)	O.D	DEA with 17 different amines	CO_2, O_2
[9]	(Blauwhoff et al., 1984)	Reaction of amines	DEA,MEA,MDEA,TEA,DIPA and so on	CO_2
[12]	(Closmann et al., 2009)	T.O + O.D	MDEA + PZ	CO_2, O_2
[13]	(Klare et al., 2000)	P.D	MDEA, DEA, MEA and so on	TiO_2, TiO_2/Pt
[20]	(Dawodu and A. Meisen, 1996)	Influence of Blends performance	MDEA + DIPA; MDEA + MEA; MDEA + DEA	CO_2
[23]	(Shahi et al., 1994)	Advantages of GC over various metd.	MDEA; DEA; MEA; MEA+MDEA; AMP	CO_2, H_2S
[30]	(Lepaumier et al., 2009c)	O.D	MDEA with 12 amines	CO_2
[31]	(Lepaumier et al., 2009b)	D	MDEA with 12 amines	CO_2
[38]	(Lawal and Idem, 2006)	Kinetics of O.D	MEA+MDEA	CO_2, O_2
[49]	(Lawal et al., 2005a)	Reaction Mechanism of D	MEA; MEA+MDEA	CO_2, O_2
[50]	(Oh et al., 2003)	D	MDEA + AMP	CO_2

O=Oxidative, T=Thermal, D=Degradation, P=Photo

2.8.1 Degradation products of MDEA and its Blend

While MDEA was initially thought of as non degradable, recently it has been shown in many articles that it will often degrade in TGTU services, and efforts are being reflected on improved reclaiming options for solvent quality control. MDEA molecule degraded into HSS, DEA, MMEA and bicine. Bis-(hydroxyethyl) glycine (Bicine) is a degradation product formed in the presence of DEA and unstable chemical intermediates. It is considered as a corrosive DGP and may be removed by vacuum distillation. It has been shown that ion exchange is not very effective in removing this compound since it is either dipolar or zwitterions. Monomethylethanolamine (MMEA) is one of the simpler amines that may be formed from MDEA degradation, since MMEA is a secondary amine, it will react directly with CO_2 and will begin to affect the performance of the MDEA solvent. Diethanolamine (DEA) is also one of the simpler secondary amines that may be formed from MDEA. Since DEA is a secondary amine, it will react directly with CO_2 and will begin to affect the performance of the MDEA solvent. Table-2.10 represents the reported degradation products of MDEA with methodology and various analytical column (packed & capillary) details.

Table 2.10: Degradation products of MDEA and MDEA-Blends

ID No.	Methodology	Column	Length × ID × Thickness	Findings
[3]	GC; GC-MS; FT-ICR/MS; NMR	Not available	Not available	Acetic, glycolic and oxalic acid nitrate, nitrite were identified; reaction mechanism of degradation
[9]	reaction between CO_2 and atkanolamines (MEA, DEA, DIPA, TEA and MDEA) in aqueous solution are discussed.			
[12]	Dionex IC/CD25/CRSR300	Dionex Ion Pac CS17	4 mm × 250mm	Resistance to oxidative degradation follows the order: MDEA/PZ> MDEA>PZ and DGP found HSS, glycolate and formate
	Dionex ICS 3000 IC	Dionex IonPac AS15)	4 mm × 250mm	
[13]	TOC, IC	Not available	Not available	Ammonium, Nitrate, nitrite
[20]	It has been shown that CO_2 loadings increase in the order DIPA < DEA < MEA and the stripping energy requirements for the blends of equal molarity increase in the order MDEA + DIPA < MDEA + DEA < MDEA + MEA. The use of aqueous blends of MDEA containing MEA, DEA or DIPA for gas sweetening operations lends to absorption equilibrium, degradation, reclamation and corrosion characteristics which are different from those of single amine solutions. The blend constituents and composition are both important in determining the characteristics.			
[23]	GC	Tenax GC (175-147 ųm) Packed column	6 ft × 1/8 in and mesh 80-100	GC is better than $BaCl_2$ and volumetric method
[30]	GC	CARBOWAX-Amines	15m × 530-ųm ×1.0-µm	4 main DGP identified
		CPSIL8-CB-Amines	25m × 320-ųm ×1.2-µm	
	GC-MS/ EI	CPSIL8-CB-Amines	30m × 250-ųm × 1.2-µm	
	GC-MS/CI	HP5-MS	30m × 225-ųm × 0.25-µm	
	NMR	N/A	N/A	
	IC	AS-15	4mm ID × 250 mm length	Oxalate, glycolate, formate, acetate, nitrate, nitrite

Table 2.10: Continued

ID No.	Methodology	Column	Length × ID × Thickness	Findings
[31]	GC	CARBOWAX-Amines	15m × 530-ųm ×1.0-µm	4 main DGP identified
		CPSIL8-CB-Amines	25m × 320-ųm ×1.2-µm	
	GC-MS/ EI	CPSIL8-CB-Amines	30m × 250-ųm × 1.2-µm	
	GC-MS/CI	HP5-MS	30m × 225-ųm × 0.25-µm	
	NMR	N/A	N/A	
	IC	AS-15	4mm ID × 250 mm length	Oxalate, glycolate, formate, acetate, nitrate, nitrite
[38]	HPLC	Shodex IC YK-421	125mm × 4.6 mm	Degradation of MEA or MEA-MDEA blends is zero at higher loading of CO_2
		Shodex IC YK-G	10 mm × 10 mm	
[49]	This papers mainly studied the degradation reaction pathways of MEA and MEA –MDEA blends induced by CO_2 and O_2			
[50]	GC (DS6200)-FID	Tenax TA 60-80 mesh	1/8 in. O.D × 9ft. long	Degradation rates and more than 15 degradation products of AMP+ MDEA were identified but didn't mention the DGP name.

2.8.2 Degradation reaction of MDEA and MDEA blend

The overwhelming advantage that MDEA currently possesses over the other amines is that, it is readily selective toward H_2S in the presence of CO_2. At high CO_2/H_2S ratios, a major portion of the CO_2 can be slipped through the absorber and into the sales gas while removing most of the H_2S. The enhanced selectivity of MDEA for H_2S is attributed to the inability of tertiary amines to form carbamates with CO_2. MDEA does not have a hydrogen atom attached to the nitrogen and cannot react directly with CO_2 to form carbamate. The CO_2 reaction can only occur after the CO_2 dissolves in water to form a bicarbonate ion, which then undergoes an acid-base reaction with the amine. At least six mechanisms for the CO_2-MDEA reaction have been proposed by Cornelissen (1982), Barth et al (1981) and Danckwerts (1979). MDEA can, however, react with H_2S by the same proton transfer mechanism of primary and secondary amines (Jou et al, 1982). There is a one CO_2 induced degradation of PZ and MDEA explained by R. Lensen (2004) and F. Closmann (2009) and are presented in the Figure 2.5 and Figure 2.6.

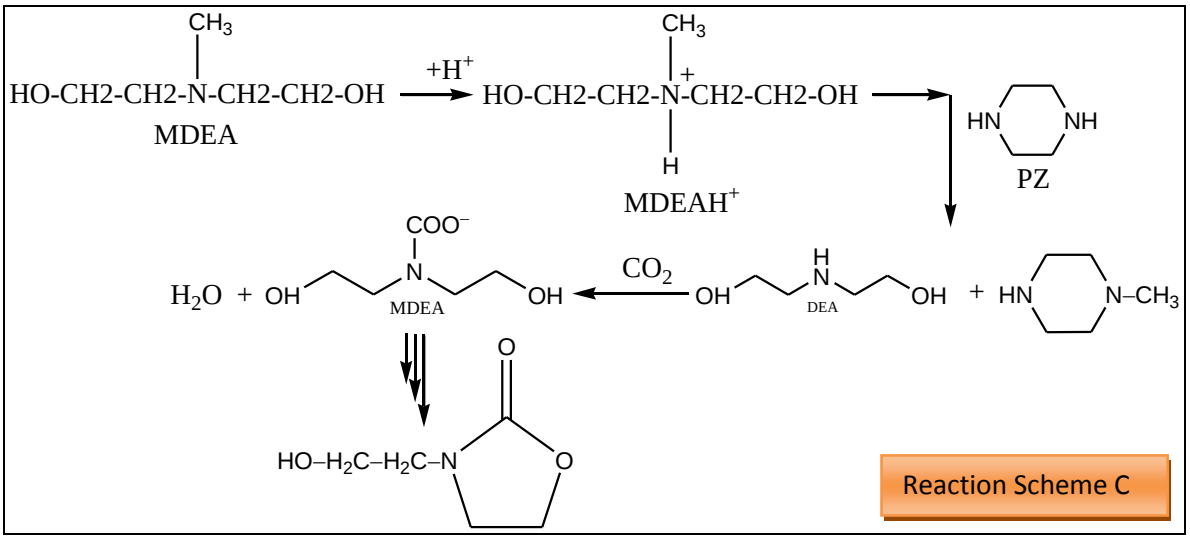


Figure 2.5: Degradation reaction mechanism of MDEA/PZ blends by (Closmann, 2009)

2.9 Degradation Study of PZ, PZ-blends and Reaction Mechanisms

In the revolution of engineering science and technology piperazine (PZ) has become the most familiar chemical in purification and in the separation process. Hence aqueous piperazine (PZ) has been investigated as a novel amine solvent for carbon dioxide (CO_2) absorption (Freeman et al., 2010). It has the viable effect on the activity of amine and alkanolamine based purification plants. PZ is a cyclic aliphatic diamine containing two substituted hydrogen atoms in its molecular structure specifically in the first and fourth positions. This H-atom is capable of reacting with other components and as a result is degraded by contaminants. Absorption reactions of PZ with CO_2 are given in the Figure 2.6 by the chemical reactions C.4 to C.7.

$$MDEA + H^+ \longleftrightarrow MDEAH^+ \quad \text{C.1}$$

$$MDEA + CO_2 \longrightarrow MDEA{\square}CO_2 \quad \text{C.2}$$

$$MEA{\square}CO_2 + H_2O \longleftrightarrow MDEAH^+ + HCO_3^- \quad \text{C.3}$$

$$PZ + CO_2 \longrightarrow PZ{\square}CO_2 \quad \text{C.4}$$

$$PZ{\square}CO_2 + H_2O \longleftrightarrow PZH+ + HCO_3^- \quad \text{C.5}$$

$$PZ{\square}CO_2 + H_2O \longleftrightarrow PZCOO^- H_3O^+ \quad \text{C.6}$$

$$PZ + H^+ \longleftrightarrow PZH^+ \quad \text{C.7}$$

$$PZ{\square}CO2 + MDEA \longleftrightarrow MDEA{\square}CO_2 + PZ \quad \text{C.8}$$

$$HCO_3^- \longleftrightarrow CO_3^{2-} + H^+ \quad \text{C.9}$$

$$H_2O \longleftrightarrow H^+ + OH^- \quad \text{C.10}$$

$$PZCOO^- + H_2O + CO_2 \longleftrightarrow PZ\,(COO^-)_2 + H_3O^+ \quad \text{C.11}$$

$$MDEA + PZOO^- + CO_2 \longleftrightarrow PZ\,(COO^-)_2 + MDEAH^+ \quad \text{C.12}$$

Figure 2.6: Reaction mechanism of MDEA/PZ (Lensen, 2004).

The degradation rate of PZ is relatively lower than MEA and DEA. Piperazine is a thermally stable compound. It has resistance to thermal degradation up to 150˚C. The resistance to oxidative degradation follows the order: MDEA/PZ>MDEA>PZ examined by (Closmann et al., 2009). Recently Freeman reported that concentrated PZ solutions showed greater resistance to oxidation compared to 7M MEA solutions (Freeman et al., 2010).

They also reported that metal-catalyzed oxidation of PZ solutions were 3–5 times more resistant to oxidation than MEA. Catalysts tested were 1.0mM iron (II), 4.0–5.0mM copper (II), and a combination of stainless steel metals (iron (II), nickel (II), and chromium (III)). Some information in this connection is illustrated in the Table-2.11.

Table 2.11: Degradation of PZ and PZ-Blends report

ID No.	Author	Major Study	Solvent	Reaction gases
[2]	(Freeman et al., 2010)	O.D + T.D	PZ	CO_2
[12]	(Closmann et al., 2009)	O.D + T.D	PZ + MDEA	CO_2, O_2
[17]	(Freeman et al., 2009)	O.D + T.D	PZ	CO_2, O_2
[43]	(Alawode, 2005)	O.D	PZ	CO_2, O_2
[44]	(Sexton, 2008)	O.D	DEA; DGA; MEA; PZ	CO_2, O_2
[48]	(Sexton and Rochelle, 2010)	O.D	MEA+PZ	CO_2, O_2

O=Oxidative, T=Thermal, D=Degradation, P=Photo

2.9.1 Degradation products of PZ and PZ-blends

The most common degradation product of PZ is HEP, BHEP, MMP, DMP and HMP (Dawodu and Meisen, 1991, 1992; Kennard M. and Axel Meisen, 1983). The above reaction mechanism already presented in the reaction scheme-D is only applicable for generic reaction and carbamat formation. Reaction mechanism illustrated by Closmann (Closmann, 2009) in the reaction scheme-C shows the path way about the formation of methyl piperazine.

Table 2.12: Degradation products of PZ and PZ-Blends

ID No.	Methodology	Column	Length × ID × Thickness	Findings
[2]	AIC (Dionex ICS-2500)/AS40	CS17	4mm × 250 mm	PZ solutions were 3–5 times more resistant to oxidation than MEA. Catalysts tested were 1.0mM iron (II), 4.0–5.0mM copper (II), and a combination of stainless steel metals (iron (II), nickel (II), and chromium (III)). Inhibitor A reduced PZ degradation catalyzed by iron (II) and copper (II).
		CG17	4mm × 50 mm	
	CIC (Dionex ICS-3000)/AS	AS15	4mm × 250 mm	
		AG15	4mm × 50 mm	
[12]	Dionex IC/CD25/CRSR300	Dionex Ion Pac CS17	4 mm × 250mm	Resistance to oxidative degradation follows the order: MDEA/PZ> MDEA>PZ and DGP found HSS, glycolate and formate
	Dionex ICS 3000 IC	Dionex IonPac AS15)	4 mm × 250mm	
[17]	AIC, CIC	Thermal degradation is negligible in concentrated PZ solutions up to a temperature of 150°C and a significant advantage over MEA systems. Oxidative degradation of concentrated PZ solutions is appreciable in the presence of copper (4 mM), but negligible in the presence of chromium (0.6 mM), nickel (0.25 mM), iron (0.25 mM), and vanadium (0.1 mM).		
	FT-IR			Volatile compounds e.g. CO_2
[43]	GC/HP5890/HP7673	HP-5 capillary column	30m	Acatate, formate, glycolate, acetone, ethanol.
	AIC/Dionex DX600	AS11 –HC/ AG 11- HC		
	NMR			
[44]	AIC Dionex ICS- 3000	AS15	4mm × 250 mm	Acetate, Glycolate, Formate, nitrate, nitrite, and Oxalate
		AG15	4mm × 50 mm	
	CIC Dionex ICS- 3000	CS17	4mm × 250 mm	
		CG17	4mm × 50 mm	
	HPLC/ELSD	T3 C18	Nonionic products HEI, HEF and DEA, a secondary ethanolamine, oxidized to form Nformyldiethanolamine, formate and other unknown HPLC products in the presence of Fe.	
	FTIR and TOC	Volatile products and total c atoms are estimated by these two methods respectively		
[48]	IC	AS 15, CS 17	Not available	Oxalate, glycolate, formate, acetate, nitrate, nitrite, EDA

2.9.2 Degradation of Miscellaneous Amines and its Blends

With regard to this major problem of amine degradation, development of new amines with higher chemical stability has become an essential prerequisite to successful plant operation. Currently more attention has been paid to polyamines (Lepaumier et al., 2010,); research seems to provide good alternatives to alkanolamines because their additional amine functions have properties similar to those of alcohols and increase CO_2 absorption capacity. Studies on degradation, reaction mechanism and blend performance of diamines and polyamines are given in Table-2.13.

Sterically hindered amines are more stable, with low degradation products and low energy consumption for the purification of degraded amine solution. Depending on this concept polyamines are considered for gas sweetening process. It can be said that those amines that are economical and considered by all conditions are taken into industrial application. Lepaumier and his co-workers investigated degraded polyamine solution and identified four main DGP so these are low cost in terms of purification (Lepaumier et al., 2010,). Same as polyamines ethanolamine and ethylenediamines (Lepaumier et al., 2009c) are partially degraded having low degradation products.

Table 2.13: Degradation report of miscellaneous amines and its blends

ID No.	Author and Year	Major Study	Solvent	Reaction gases
[3]	(Lepaumier et al., 2009a)	O.D	EDA with 17 different amines	CO_2, O_2
[9]	(Blauwhoff et al., 1984)	Reaction of amines	DEA,MEA,MDEA,TEA,DIPA and so on	CO_2
[14]	(Klare et al., 1999)	P.D	Amine compounds	TiO_2/UV
[20]	(Dawodu and A. Meisen, 1996)	Influence of Blends performance	MDEA + DIPA; MDEA + MEA; MDEA + DEA	CO_2
[30]	(Lepaumier et al., 2009c)	O.D	DEA with 12 amines	CO_2
[31]	(Lepaumier et al., 2009b)	D	DEA with 12 amines	CO_2
[35]	(Lepaumier et al., 2010,)	O.D + T.O	Polyamines	CO_2

O=Oxidative, T=Thermal, D=Degradation, P=Photo

Table 2.14: Degradation products and characterization methods of miscellaneous alkanolamines and its blends

ID No.	Methodology	Column	Length × ID × Thickness	Findings
[3]	GC; GC-MS; FT-ICR/MS; NMR	Not available	Not available	Acetic, glycolic and oxalic acid nitrate, nitrite were identified; reaction mechanism of degradation
[9]	Reaction between CO_2 and atkanolamines (MEA, DEA, DIPA, TEA and MDEA) in aqueous solution are discussed.			
[14]	TOC/ASI-5000	Total concentration of organic carbon changes monitored by this test		
	AIC	IC-AN	Not available	Nitrate and nitrite are identified
	CIC	IC-CA	Not available	Short chain alkyl / alkanolamines and ammonium were detected
[20]	It has been shown that CO_2 loadings increase in the order DIPA < DEA < MEA and the stripping energy requirements for the blends of equal molarity increase in the order MDEA + DIPA < MDEA + DEA < MDEA + MEA. The use of aqueous blends of MDEA containing MEA, DEA or DIPA for gas sweetening operations lends to absorption equilibrium, degradation, reclamation and corrosion characteristics which are different from those of single amine solutions. The blend constituents and composition are both important in determining the characteristics.			

Table 2.14: Continued

ID No.	Methodology	Column	Length × ID × Thickness	Findings
[30]	GC	CARBOWAX-Amines	15m × 530-ųm ×1.0-µm	4 main DGP are identified
		CPSIL8-CB-Amines	25m × 320-ųm ×1.2-µm	
	GC-MS/ EI	CPSIL8-CB-Amines	30m × 250-ųm × 1.2-µm	
	GC-MS/CI	HP5-MS	30m × 225-ųm × 0.25-µm	
	NMR	N/A	N/A	
	IC	AS-15	4mm ID × 250 mm length	Oxalate, glycolate, formate, acetate, nitrate, nitrite
[31]	GC	CARBOWAX-Amines	15m × 530-ųm ×1.0-µm	4 main DGP are identified
		CPSIL8-CB-Amines	25m × 320-ųm ×1.2-µm	
	GC-MS/ EI	CPSIL8-CB-Amines	30m × 250-ųm × 1.2-µm	
	GC-MS/CI	HP5-MS	30m × 225-ųm × 0.25-µm	
	NMR	N/A	N/A	
	IC	AS-15	4mm × 250 mm length	Oxalate, glycolate, formate, acetate, nitrate, nitrite
[35]	GC	CARBOWAX-Amines	15m × 530-ųm ×1.0-µm	4 main DGP identified for each polyamines. The author also found that tertiary amines were more stable but it is not always true: four tertiary polyamines DMP, TMEDA, TMPDA, and PMDPTA were shown to be more stable than MEA while two tertiary polyamines (TMBDA and PMDETA) are much less stable than MEA.
		CPSIL8-CB-Amines	25m × 320-ųm ×1.2-µm	
	GC-MS/ EI	CPSIL8-CB-Amines	30m × 250-ųm × 1.2-µm	
	GC-MS/CI	HP5-MS	30m × 225-ųm × 0.25-µm	
	NMR	N/A	N/A	
	IC	AS-15	4mm ID × 250 mm length	Oxalate, glycolate, formate, acetate, nitrate, nitrite
	FT-ICR/MS	For higher molecular weight compound identification		

2.10 Most probable degradation products of amines and amines blends

The most probable degradation products of alkanolamine were found in the open literature. The polymeric degradation products are still nor well understood. The higher molecular weight compounds were identified by HPLC and GCMS and the lower one is by IC both in anionic and cationic analysis.

Table 2.15: Typical example of degradation products of amine and alkanolamine

Amine and amine blends	Possible DGPs
MDEA and/ MDEA/PZ	EG, HMP, DEA, TEA, BHEP, DMAE, MPZ, DMPZ, $DEACOO^{-}$, $MDEAH^{+}$, Polymers
DEA	MEA, HEM, HEED, DEA, HEP, OZD, TEA, BHEED, BHEP, HEOD, HEI, THEED, BHEI, THEED, MEACOOH, DEACOOH, AEEA, ETAHEAME, EAE, TSIM
MEA	OZ, HEIA, HEEDA, MEA urea, Polymers
PZ	$PZCOO^{-}$, $PZ(COO^{-})2$, $H^{+}PZ$, $H+PZCOO^{-}$, DMPZ, MPZ
Miscellaneous DGPs	$DEACOO^{-}H^{+}$, $MEACOO^{-}H^{+}$, $DEACSS^{-}H^{+}$, $DEACSS^{-}$, $DEAH^{+}$, EDA, Glycolate, Formate, Acetate, Oxalate, Nitrate, Nitrite, Formamide, Oxamide

2.11 Research gap available in the open literature

Literature cited sufficient information on the degradation of amine and alkanolamines induced by carbon dioxide, H_2S, COS, CS_2 and O_2 but most of these work conducted at higher temperature and for long duration. Rochelle group emphasis the degradation of MEA during the flue gas treatmet process and A. Meisen conducted research work on DEA individual solution particularly in natural gas purification process induced by CO_2, COS and CS_2. P. L. Careette research group specially conducted research on the identification and degradation mechanism for several group of amines particularly on monoamine, diamine induced by carbon dioxide. Degradation products of MDEA/PZ blends were conducted by Fremann et al., in 2009 but some DGPs are still unknown. To the best of our knowledge degradation studies of DEA/PZ have not yet been studied and there are no information about DEA/PZ induced by any sour gas components was found. In addition some amines e.g. TBEE, DIPA, DGA and TEA were used in the aqueous absorption process as replacement of primary alkanolamines like MEA, DEA and MDEA. However these amines are yet to be characterized for their DGP's. Several chromatographic methods were carried out for the characterization of degradation products nevertheless no specific method was found for these particular amines even though particular solvent or chromatohraphic column. Most of the degradation studies of alkanolamine were conducted under particular temperature but the clues of identification are not explained in some cases.

CHAPTER 03

METHODOLOGY

CHAPTER THREE: METHODOLOGY

This chapter describes the experimental apparatus and procedure for the carbon dioxide induced degradation of carbonated solution of DEA and MDEA and their blends with PZ. Details of the equipment, chemicals, solution preparation, typical experimental run and analysis will be given in the following representation. In addition, this chapter deals with a description of the analytical equipments and analytical procedure. To identify the degradation products, Ion Chromatography (IC), Gas Chromatography Mass Spectrometer (GC-MS) and High Performance Liquid Chromatography (HPLC) were analyzed to detect unknown reaction products.

3.1 Chemicals

PZ, DEA and MDEA (reagent grade, 99% purity) were purchased from Mercks Chemical Company, Germany. Few of the samples are purchased from Fischer Scientific and rest of the chemicals and analytical standards are imported from Sigma Aldrich, Germany which particularly listed in the appendix A. Hydrochloric acid of concentrations (1M and 2M) purchased from Mercks chemical company. The list of chemicals is given in the appendix A with details informations like molecular formula, product ID and identity etc.

3.2 Sample Preparation

Aqueous alkanolamine solution is prepared using distilled water (DW) to the predetermined concentration. The solution's concentration will then be determined by titration with standard 1.0 M and 2.0 M HCl reagent so that the exact concentration was ascertained. Necessary precautions should be taken to avoid any exposure of the sample to the air during the preparation period. The following amine solutions of various concentrations were prepared for five systems (i-v).

PZ-H_2O [1M, 2M] ……..……. i

DEA-H_2O [2M, 3M, 4M] …….……. ii

MDEA-H_2O [2M, 3M, 4M] …….. iii

DEA-PZ-H_2O [4M, 6M, 7M, 8M, 11M] …….. iv

MDEA-PZ-H_2O [4M, 6M, 7M, 8M, 11M] …….. v

Eighteen different amine samples were prepared for the above mentioned five systems. Each solution is degraded individually induced by CO_2 and characterized in order to get degradation products and physical properties.

3.3 Flowdiagram of Overall Experimental Setup and Analysis

The prepared alkanolamine solutions are prepared by using volumetric flsk according to the predetermined concentrations as mentioned in the section 3.2 (Equ. I-V). These dilute virgin amine solutions are degraded and labeled with code numbers as given in the table 3.1. The degraded solutions are diluated and characterized by chromatographic methods and indentify the degradation products. On the otherhand the degraded solutions are directly used inorder to characterize physical properties such as density, viscosity, loading and pH without dilution. The following Figure 3.1 will give us clear concept about the successive steps which were done in this research.

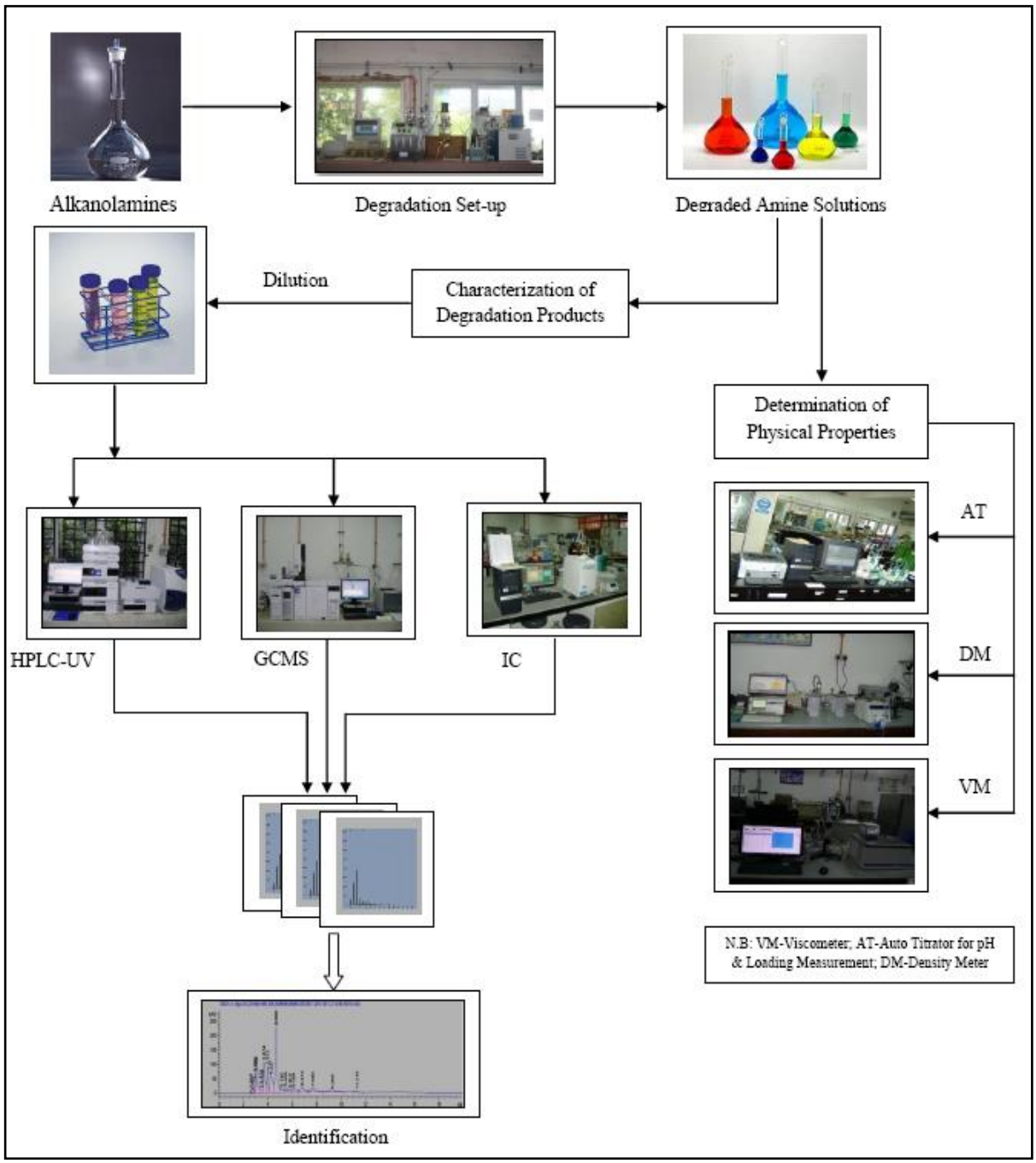


Figure 3.1: Schematic diagram of overall experimental work and analysis

3.4 Equipments

3.4.1 Degradation Equipment and Setup

The degradation experiments were conducted in 1.0L glass jacketed (borosilicate 3.3 @ pyrex) reactor equipped with stainless steel 316L top plate, stainless steel impeller, top plate lip seal (Top and Bottom), stainless steel shaft bearing with stirrer shaft, stainless steel glass vessel holder. The reactor is designed with bottom sample outlet PTFE valve. An analogue pressure meter, Digital pH meter, Pt-100 temperature probe and digital display of pressure are built on the top plate of the reactor for measuring reactor's interior pressure, pH and temperature. Overhead stirrer motor is capable of agitation speeds of up to 1500 rpm with overheat protection, digital display and digital PID control of RPM is built in the central position of top plate. A stainless steel condenser (comes with built in coil) with inlet, outlet and exhaust point which is used for the loose solution evaporation under high temperature. A stainless steel ring spurger comes with top head lock, top plate vinton circular ring, top head stainless steel plug circular ring are equipped with the reactor for proper distribution of carbon dioxide during degradation reaction. The heat supplied to the reactor is controlled by a temperature indicator controller system equipped with a J-type thermocouple. Temperature is measured by a J-type thermocouple and controlled by RSC LAUDA R22 type water circulator. A digital pressure transducer is used to measure the total pressure in the reactor and a pH probe linked to Metrohm^{R} 719S auto-titrator is used to monitor and record the pH of the solution versus time which is controlled by Tinet^{R} software. The feed gases are forced through the reactor sample by using a set of Brooks^{R} gas mass flow meters model 5850C for CO_2 and controlled by a 4 channel Brooks's mass flow controller model 0154E. Gas supply system into the reactor is also forced by needle valve flow meters to check the flow accuracy; these are mounted on the stainless steel control cabinet.

Before introducing the gases into the reactor it is first forced into the water saturator and conditioned at experimental temperature to avoid any deviation with reactor temperature. The temperature accuracy of the controller was within 0.1%. A schematic diagram of the experimental setup is shown in the Figure 3.2 and Figure 3.3.

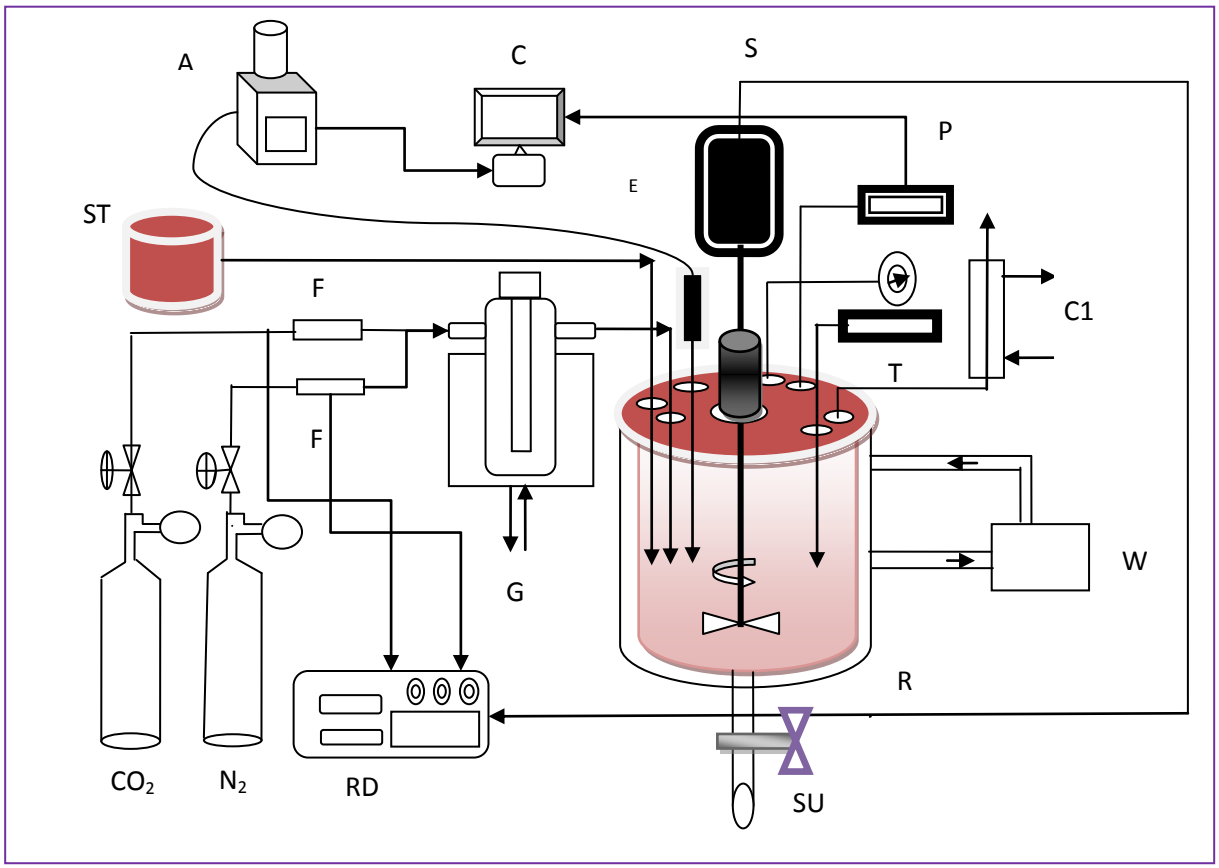


Figure 3.2: Schematic diagram for the degradation study of activated amine solution.

Here, W=Water bath; C1=Gas outlet and Condenser; A=Autotitrator for continuous observation of pH with time; E=Electrode connected with autotitrator; F=Flow meter; P=Pressure sensor; T=Digital thermometer; S=Stirrer [~1500 rpm]; ST= Solvent storage tank and Inlet; RD= Regulator and display; C=Computer for data collection; G=Gas saturator and heater; SU=Sample outlet for analysis; R=Jacketed glass reactor [1L].

Figure 3.3: Laboratory experimental setup for the degradation study of activated amine solution.

3.4.2 Autotitrator

In order to determine the amine concentration and carbon dioxide loading of virgin and degraded amine solutions titrimetric methods was used. During the experiment titration was done using metrohm Autotitrator. The equipment model is A785 DMP Titrino. This autotitrator equipped with computerized system were as Titrino software is used to run the analysis. The experimental setup of autotitrator was shown in figure 3.4.

Figure 3.4: Metrohm autotitrator setup with Tiamo software

3.4.3 Viscometer

The viscosity was measured using a BROOKFIELD LV SC4-18 viscometer. The solutions were charged into jacketed vessel that was connected to thermostated bath. The bath temperature was controlled within (0.1 K) of set temperature with a circulator temperature controller. A typical view of this viscometer was given in the Figure 3.5.

Figure 3.5: A Typical view of BROOKFIELD (LV) Viscometer

3.4.4 Density Meter

The densities of the amine solutions were measured using an Anton Paar DMA 4500 density meter. The temperature of the solution was controlled within 0.2 K of the desired temperature using an internal temperature controller. The equipment's picture was shown by the Figure 3.6.

Figure 3.6: A Typical view of Anton Paar (DMA 4500) Density Meter with automatic software

3.4.5 High Performance Liquid Chromatography (HPLC)

The HPLC instrument used for analysis of the liquid samples was equipped with a UV detector of model number 1200/G1312B, Agilent Technologies, USA. An auto sampler (Model G1313A, Agilent Technologies, USA) was used for sample introduction. The picture of this equipment's shown in the Figure 3.7.

Figure 3.7: High Performance Liquid Chromatography (HPLC)

3.4.6 Gas Chromatography Mass Spectroscopy (GC-MS)

Analysis of the samples was carried out using a gas chromatography-mass spectrometer (GC-MS) of model number G3171A and auto sampler of model 7693 supplied by Agilent technology. Figure 3.8 shows the GC-MS equipment used in this work.

Figure 3.8: Gas Chromatography Mass Spectrometer (GC-MS)

3.4.7 Ion Chromatography (IC)

Ion chromatography was performed using a Metrohm 861 Compact IC instrument with suppressed and non-suppressed detection (Model 861 Avanced Compact IC, Methrom, Switzerland). The IC was equipped with a dual-piston pump, 863 compact autosampler, a degas assembly, and digital conductivity detection. Data processing was performed with IC Net 2.3 software. The Figure 3.9 shows the picture of the used IC equipment used in this work.

Figure 3.9: Professional Compact Metrohm Ion Chromatography

3.5 Experimental Methods

3.5.1 Degradation Procedure

Typically, 1000 ml of an aqueous amine solution was placed in the reactor. Before purging gas through the reactor all control modules are turned on according to the preselected control parameters. The stirrer was set to a speed of 1200 rpm and oxygen was purged out from the reactor by passing nitrogen through the amine solution for ≈25 to 30 min. Then a known volume of 100 % pure CO_2 was forced into the reactor from a stainless steel cylinder which was connected to the reactor. Gas flow rates ranged up to 200 cc/min. The gas inlet valve was left open for a month till completed 6 cycles for each designed sample. In each cycle, liquid samples were withdrawn during absorption and desorption process to be analyzed for characterization. The absorption and desorption experiments were performed at 55°C and 100˚C respectively. There are six generic cycles that were conducted for each amine solution of eighteen. For each cycle 50 ml of sample withdrawn from the reactor and the CO_2 loading, concentration was then quantified by liquid-phase analysis of the total dissolved CO_2. Carbon dioxide for absorption and desorption process is referred to as rich and lean loading respectively. The reaction of CO_2 with amine solvents causes a decrease in alkalinity. Thus, the variation of pH of the solution is monitored continuously with time, until the equilibrium is reached. When the equilibrium is reached in case of absorption and desorption process then the experiment is stopped for each cycle. Figure 3.10 represents a typical variation of solution's pH with time.

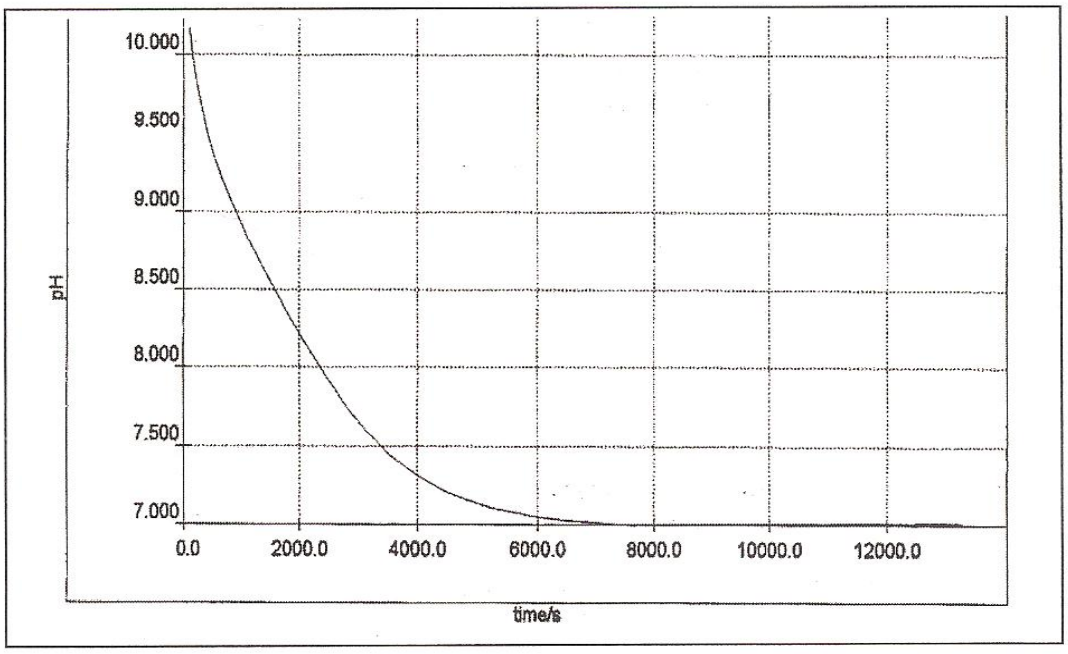


Figure 3.10: Variation of pH with time during the absorbtion reaction of CO_2 with alkanolamine

In case of desorption process the pH curve shows the opposite trends of absorption process. The pH is increased till to equilibrium reached. Generally at pH 10-11 the equilibrium curve is shown. Figure 3.11 represents the variation of pH with time during the desorption process.

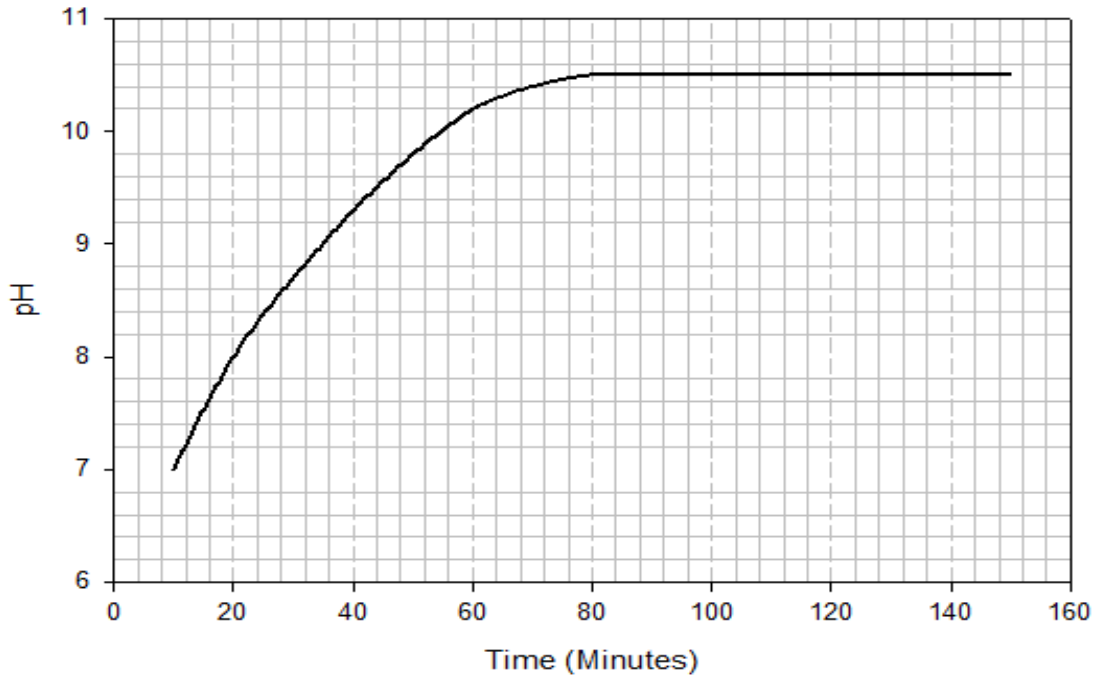


Figure 3.11: Variation of pH with time during the desorption reaction of CO_2 with alkanolamine

3.5.2 Experimental Runs of Five Degradation Systems

3.5.2.1 PZ-H_2O-CO_2 Systems

There are two different types of samples (1M and 2M) were prepared of this system. It is about 1000 mL of these two samples were introduced into the reactor two times gradually and conducted degradation reaction with CO_2 for two weeks to accomplish six cycles. Process parameters e.g. temperature, pressure, gas flow rate, stirring rate, pH meter are turned on and settled as predetermined process parameters accordingly. The temperature was settled 55˚C and 100˚C for absorption and regeneration process respectively. CO_2 partial pressures is measured at 100 100 kPa. The gas flow rate is maintained through the reactor is about 200 cc/min. The stirrer was settled at the rate of 1200 rpm. When the reaction mixture reached at the desired temperature, the pressure is noted and added CO_2 gas through the amine solution to get the desired equilibrium**.** When the equilibrium is reached, an aliquot of 50 mL sample is taken from each experimental run in case of absorption and regeneration. The collected samples are labeled with ID and stored for further analysis. The degraded two types of samples were leabeled using these two code number D01PZ1M and D02PZ2M. These samples are used to analyze amine concentration, degradation products, CO_2 loading, density and viscosity.

3.5.2.2 DEA-H_2O-CO_2 Systems

In this degradation studies three different types of inactivated samples of concentration (2M, 3M and 4M) were prepared. It is about 1000 mL of these three samples were introduced chronologically into the reactor and conducted their individual degradation reaction with CO_2 for two weeks to accomplish six cycles. The same precaution, process parameters were applied in these degradation studies of inactivated DEA samples which were described in section (3.5.2.1).

The degraded reaction samples are collected after definite periods of absorption and desorption process. The sample was taken at the time of six cycles for each solution's and labeled using these sample codes D03DEA2M, D04DEA3M and D05DEA4M respectively as mentioned above. Then it was labeled and stored at recommended condition for further analysis.

3.5.2.3 DEA-PZ-H_2O-CO_2 Systems

Degradation studies of activated DEA, Five different types of samples were prepared of this system. The degraded sample's codes of this system for five samples are D06DEA2MPZ1M, D07DEA2MPZ2M, D08DEA3MPZ2M, D09DEA4MPZ2M and D10DEA7MPZ2M. Typical experimental run ID is D06, D07, D08, D09 and D10 for the above mentioned samples. The same experimental procedure and parameters were applied during the degradation study of activated diethanolamine (DEA) solution. Degraded solutions are used for further analysis like IC, GC-MS and HPLC in order to detect occurred degradation products.

3.5.2.4 MDEA-H_2O-CO_2 Systems

In this degradation system three different types of inactivated samples were prepared. It is about 1000 mL of these three samples were introduced chronologically into the reactor and conducted their individual degradation reaction with CO_2 for two weeks to accomplish six cycles. The same precaution, process parameters are applied in these degradation studies of inactivated MDEA samples which explained in the above section (3.5.2.1). Finally degraded samples were labeled and stored for further chromatographic analysis in order to characterize DGPs. Sample labeling was done using using these codes i.e. D11MDEA2M, D12MDEA3M and D13MDEA4M.

3.5.2.5 MDEA-PZ-H_2O-CO_2 Systems

Degradation studies of activated MDEA, Five different types of samples were prepared of this system. The each solution is degraded and after degradation samples are labeled using these code numbers i.e. D14MDEA2MPZ1M, D15MDEA2MPZ2M, D16MDEA3MPZ2M, D17MDEA4MPZ2M and D18MDEA7MPZ2M. Typical experimental runs ID numbers for these five samples are D14, D15, D16, D17 and D18 for the above mentioned samples. During the degradation study the same experimental procedure and parameters were applied as explained above. The resultant degraded solutions were used for further analysis like IC, GC-MS and HPLC to detect occurred degradation products.

3.5.2.6 Labeling of Degraded Reaction Sample

In this entire study there are eighteen typical experimental runs (D01-D18) were conducted during degradation experiment for eighteen different concentrated solutions of five degradation systems. After degradation all samples were leveled using given code numbers which shown in the Table 3.1. Each degraded sample was analyzed inorder to get information regarding DGPs and physical properties like density, viscosity, carbon dioxide loading and concentration etc were also investigated.

Table 3.1: Componets of formulated amine samples and code numbers of degraded reaction samples used for labeling

T. Ex. Run	Solvent+Solute	Amine (AM)	[AM]	Activator (AC)	[AC]	[Sol]	Sample Code
D01	DW+AC	--	--	PZ	1M	2M	D01PZ1M
D02	DW+AC	--	--	PZ	2M	4M	D02PZ2M
D03	DW+AM	DEA	2M	--	--	2M	D03DEA2M
D04	DW+AM	DEA	3M	--	--	3M	D04DEA3M
D05	DW+AM	DEA	4M	--	--	4M	D05DEA4M
D06	DW+AM+AC	DEA	2M	PZ	1M	4M	D06DEA2MPZ1M
D07	DW+AM+AC	DEA	2M	PZ	2M	6M	D07DEA2MPZ2M
D08	DW+AM+AC	DEA	3M	PZ	2M	7M	D08DEA3MPZ2M
D09	DW+AM+AC	DEA	4M	PZ	2M	8M	D09DEA4MPZ2M
D10	DW+AM+AC	DEA	7M	PZ	2M	11M	D10DEA7MPZ2M
D11	DW+AM	MDEA	2M	--	--	2M	D11MDEA2M
D12	DW+AM	MDEA	3M	--	--	3M	D12MDEA3M
D13	DW+AM	MDEA	4M	--	--	4M	D13MDEA4M
D14	DW+AM+AC	MDEA	2M	PZ	1M	4M	D14MDEA2MPZ1M
D15	DW+AM+AC	MDEA	2M	PZ	2M	6M	D15MDEA2MPZ2M
D16	DW+AM+AC	MDEA	3M	PZ	2M	7M	D16MDEA3MPZ2M
D17	DW+AM+AC	MDEA	4M	PZ	2M	8M	D17MDEA4MPZ2M
D18	DW+AM+AC	MDEA	7M	PZ	2M	11M	D18MDEA7MPZ2M

N.B: [AM]-Amine Concentration, [AC]-Activator Concentration, [Sol.]- Solution's Concentration

3.5.3 Analysis of Physical Properties of Degraded Reaction Solutions

The physical properties of degraded amine solutions such as carbon dioxide loading, density, viscosity and pH were determined for virgin and degraded condition and studied the variation of these properties with time, temperature and concentrations. The details procedures of these measurements were given in the following sections.

3.5.3.1 Determination of CO_2 Loading

An aliquot of three 10 ml samples were taken from the reactor and mixed with an excess of a mixture of 1M barium chloride solution and 1M sodium hydroxide solution. The samples are kept on heated magnetic stirrer at a temperature of 70^{o}C and atmospheric pressure for 3 hours. This mixture is used to convert all free dissolved gas into non volatile ionic species and to precipitate all carbon dioxide in the carbonated amine solution as white barium carbonate crystals. The mixture is settled, filtered and washed with distilled water then titrated with 1M HCl using a PC controlled Metrohm^{R} 716 DMS autotitrator and by applying dynamic equivalent end point titration technique for the determination of End Point. A typical titration curve is shown in Figure 3.12.

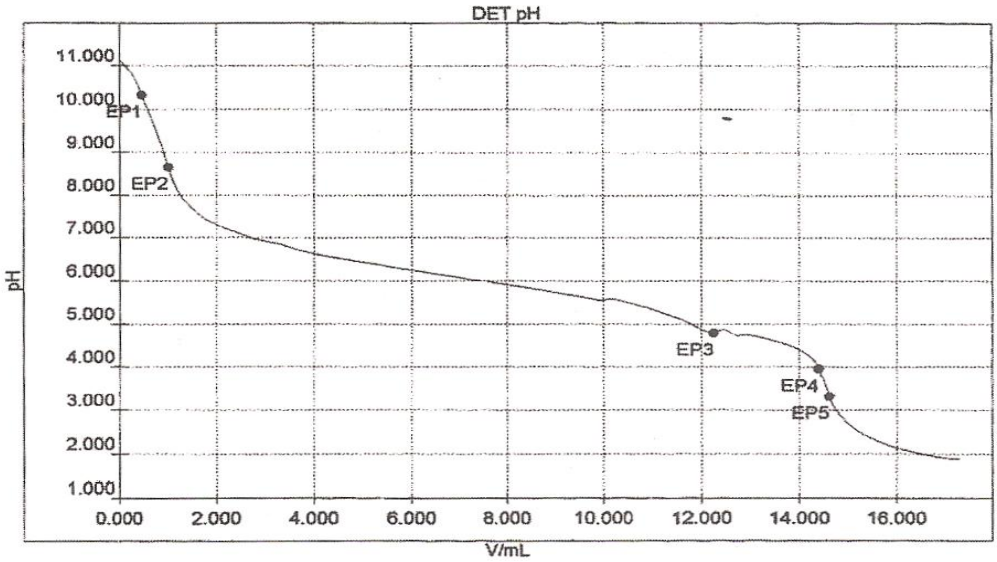


Figure 3.12: Variation of pH with 1 M HCl during the titration of the sample

The volume of HCl used to neutralize the carbonate is determined using the first derivative of the titration curve. The loading is then calculated according to the following equation.

$$\alpha = \frac{V_{HCl}}{V_{Sample} \times 2M} \ldots\ldots\ldots\

3.5.3.2 Determination of Amine Concentration

In the beginning of the experiment during the preparation of amine sample all prepared samples which are given in the Table 3.2, their concentrations were determined using the Metrohm autotitrator. At the end of the each typical experimental run an aliquot sample of 10 ml of carbonated amine is titrated with 1 M HCl to check on the final amine concentration. It is noted that high concentration amine samples are titrated using 2M standard HCl solution during the analysis.

3.5.3.3 Determination of Solution Viscosity

The Brookfield DV-II+ Pro EXTRA viscometer measures fluid viscosity at given shear rates. It is configured with Brookfield software, Rheocalc V3.2 which is controlled by the computer. This viscometer is also set to the external control mode to allow for proper communication with Rheocalc. To control the temperature it is configured with digital bath system which model is TC-502. The used spindle model is 13RP which is adjusted with the viscometer with right speed and time. The speed is given LV commend during measurement. To get the automatic printed results a printer is also connected with this computing system. During the measurement of viscosity the viscometer is put on the stand tightly and then RTD probe is connected to the socket on the rear panel of the DV-II+ Pro EXTRA. The Viscometer must be leveled during setting. The level is adjusted using the two leveling screws on the base. Adjustment is done so that the bubble level on top of the viscometer is centered within the circle.

After that the red shipping cap is removed which covers the EZ-Lock spindle chuck on the Viscometer. During the setting period, AC power switch is turned OFF, after that the power cord is connected to the socket and plug into the appropriate AC line. After installing every part of the viscometer the power switch is turned to the ON position and allowed to warm up for 10 minutes before performing auto zero.

When the machine is ready to use, about 5-6 ml amine samples are taken into the sample chamber and put the spindle into the chamber in such a way that no sample is over flooded. The sample chamber is adjusted with stand and click on the Rheocalc V3.2 software icon and press start then automatically the measured viscosity is displayed which is noted and recorded for information.

3.5.3.4 Determination of Solution Density

Anton Paar DMA 4500 is a digital density meter, which configured with a printer and pump to inject the sample in to the measuring cell/chamber of the equipments. It is also configured with a temperature controller, in order to measure the density at different temperature. This test is conducted under normal atmospheric pressure. During the measurement of solution's density, amine samples are filled about 8 to 10 mm below the rim and place them into the magazine, starting at position 1. The special Teflon cover is then placed with a hole in the center onto the filled amine sample vials. The magazine is turned to the zero position by pressing the "0" key. Press the "START" key at the SP-1m. After pressing the "START" key the magazine is turned to the first vial. When the last vial is filled then the magazine is automatically turned to zero position. The measuring procedure is interrupted by pressing the "STOP" key at the SP-1m in any time during test. After pressing the "START" key, the measuring procedure is continued at the following vial.

A printer is activated and connected to the DMA 4500 density meter, a printout is occurred after each sample has been measured. The printed results are noted and recorded for information. Some precautions are maintained in this test analysis i.e. no empty sample is put in the magazine and no sample is left in the measuring cell, while the SP-1m is not in operation.

3.5.4 Chromatographic Analysis of Degraded Reaction Sample

3.5.4.1 Ion Chromatography (IC)

Three different modes of chromatography (anion exchange, cation exchange and ion exclusion) were used in this investigation which simply relate to the different types of columns used to achieve the separation of the ions. The eluent used depends on the column type and also the mode of detection.

3.5.4.1.1 Anion Exchange Chromatograpgy

In anionic ion chromatographic method (AICM) before analyze samples the equipment is properly connected with tubing and installing the column. To prevent the analytical column from high pressure a gurad column is also installed through the system. The analytical column and guard column of this method are used Metrosep A Supp 5 150/4.0 (6. 1006. 520) and Metrosep A Supp. 4/5 Guard (6. 1006. 500). Both columns are installed without any conditioning generally operated at ambient temperature. After completing the IC instrumental setup according to AICM then it is turn on and switch on the computer and open IC net 2.3 software icone. Inorder to remove air bubble and old eluent from the instruments and aspirating tubing the system is flashed with UPW for 40 minutes. The required amount of eluent of concentration 0.1M is prepared from a mixture of Na_2CO_3 and $NaHCO_3$ using UPW on daily basis. Then 100mM H_2SO_4 solution was prepared for suppression regeneration. After flashing, the eluents and suppression solutions are transferred into the tubing bottles and set on the right position of IC. The IC machine is kept turn on for 45 to 1 hour till to get desired flow rate, conductivity and operating pressure which are given in the table 3.2. Degraded amine solutions are diluated using UPW with diluation ratio 1:40 (amine:water) and filtrated by 0.2 µm PTF filter. Then filtrated solutions are filled in IC vials and labelled according to the sample code number as well as arrange in the autosampler. This is mentioned that during the sample arrangement into the autosampler tray first and last four samples vials must be filled by UPW.

When the operating condition is reached then the autosamplers is turn on. About 10µL samples are injected into the IC for detection. The analysis time is set about 20 minutes for each sample. In this way IC standards are prepared and analyzed first in ordr to do the calibration and characterization of anionic degradation products.

Table 3.2: Operating condition and solvent of IC method for anion analysis

Method	Parameters	Conditions
AICM	Column	Metrosep A Supp 5 150/4.0 (6. 1006. 520)
	Guard Column	Metrosep A Supp 4/5 Guard (6. 1006. 500)
	Eluent	Na_2CO_3+$NaHCO_3$ [0.1M]
	Flow Rate	0.5-0.7 ml/min
	Temperature	Ambient 25 ˚C
	Detector	Suppressed conductivity
	Inj. Volume	10 ml
	Analysis Time	20 min
	Solvent for Suppressor regeneration	H_2SO_4 (100 mM)
	Pressure	6.00-9.00 MPa (6.4 MPa)
	Conductivity	13-17 µS/cm

3.5.4.1.2 Cation Exchange Chromatography

Cation analyses were carried out using the same IC equipment. CICM is a non suppression detection process. Priror to analysis analytical columns are properly installed and eluent is prepared. The eluent is used in ths method is a mixture of 1.7 mM HNO3 + 0.7 mM dipicolinic acid. Since this method is a non suppression method so no solvent is used for suppression regeneration. The analytical column and guard column of this method are used Metrosep C Supp 4 150/4.0 (6. 1050. 420) and Metrosep C4 Guard (6.1050.500) respectively. Both columns do not need conditioning operated at ambient temperature. Priror to start analysis make sure that the equipment is properly connected with aspirating tubing and installing the column without leakage. After completing the IC instrumental setup according to CICM then it is turned on and switch on the computer and open IC net 2.3 software icon. In order to remove air bubble and old eluent from instruments and aspirating tubing it is flashed with UPW for 40 minutes. After flashing, the eluents is transferred into the tubing bottles and set to the right position of IC. The IC machine is kept turn on for 45 to 1 hour to get desired flow rate, conductivity and operating pressure which are given in the table 3.3. It takes normally one and half hours for stabilizing and adapting the IC equipments to run the sample. The sample preparation and typical experimental run are the same as AICM. Degraded amine solutions are diluted using UPW with diluation ratio 1:40 (amine: water) and it is filtred by 0.2 µm nylon filter. Then filtrated solutions are filled in IC vials and lebelled with sample code number and arrange in autosampler. This is mentioned that during the sample arrangement into the autosampler tray first two and last two must be filled by UPW. When the all operating condition is reached then autosampler is turned on and about 10µL samples are injected into the IC for detection. The analysis time is set about 20 minutus for each sample. During the sample analysis standards are run at first and calibrated then amine samples are analyzed to detect cationic species.

Table 3.3: Operating condition and solvent of IC method for cation analysis

Method	Parameters	Conditions
CICM	Column	Metrosep C Supp 4 150/4.0 (6. 1050. 420)
	Guard Column	Metrosep C 4 Guard (6. 1050. 500)
	Column Dimension	Length 150.00 mm, ID 4.0 mm
	Eluent	1.7 mM HNO3 + 0.7 mM Dipicolinic Acid
	Flow Rate	0.9-1.00 ml/min
	Temperature	25.0 ˚C
	Detector	Non-suppressed conductivity
	Inj. Volume	10.0 ml
	Analysis Time	20 min
	Solvent for Suppressor regeneration	UPW
	Pressure	0.4 MPa (6.4 MPa)
	Conductivity	0.831µS/cm

3.5.4.1.3 Ion Exclusion Chromatography (IEC)

Ion exclusion chromatography (IEC) is mainly used for the separation of weak acids or bases. The greatest importance of IEC is for the analysis of weak acids such as carboxylic acids, carbohydrates, phenols or amino acids. In this experiment carboxylic acids are mainly investigated using the same IC equipments. Metrosep Organic Acids (6.1005.200) analytical column of dimention length 250 mm and ID 17.8 mm is used. To protect this column from high pressure and liquid flow a guard column Metrosep Organic Acids Guard (6.1005.250) is used. Priror to the analysis both columns are installed and the eluent 0.5×10^{-3} M H_2SO_4 is prepared. Since OICM is suppression detection method so 0.01 M LiCl is also prepared as suppression regeneration solvent. When the aspirating tubing system, column installation, regeneration solvent preparation and elution preparation are completed then IC machine and computer is turn on. Then IC net 2.3 software is opened and given proper commend for flasing and analysis successively. In order to remove air bubble and eluents from previous user through the aspirating column the whole system is flashed for 40 minutes using UPW. After flashing, the eluents and suppression solvent placed in the respective solvent bottle and connected with tubing. In order to start the sample analysis the system is required to be stabilized. The stabilization is done followed by desired conductivity, pressure and solvent flow rate which are given in the table 3.4. In this purpose the system is turn on for one and half hour. When the desired condition for stabilization is reached then the sample analysis is started. The sample preparation and analysis are same for all chromatographic system other than operating condition, analytical column and stabilization condition. The sample injects volume and analysis times are also same as with AICM and CICM.

Table 3.4: Operating condition and solvent of IC method for organic acids analysis

Method	Parameters	Conditions
OICM	Column	Metrosep Organic Acids (6.1005.200)
	Column Dimension	Length 250 mm × 17.8 mm
	Guard Column	Metrosep Organic Acids Guard (6.1005.250)
	Eluent	0.5×10^{-3} M H_2SO_4
	Flow Rate	0.5 ml/min
	Temperature	25.0 ˚C
	Detection	Suppressed conductivity
	Inj. Volume	10 ml
	Analysis Time	20 min
	Regeneration Solvent	0.01 M LiCl
	Pressure	6.00-9.00 MPa (6.4 MPa)
	Conductivity	13-17 µS/cm

3.5.4.1.4 Preparation of IC standard solutions

All standard solutions were prepared separately using ultra pure water (UPW) for the five degradation systems. In cationic ion chromatographic method (CICM) protonated amines e.g. monoethanolamine (MEA), diethanolammine (DEA), methyldiethanolammine (MDEA), piperazine (PZ) and ammonium ion are prepared and calibrated in order to detect cation. For AICM method the standard solutions of phosphate, nitrate, nitrite, carbonate, acetate and formate are prepared and calibrated. During the calibration five different concentrations are prepared. In case of OICM, four anionic standards solutions of format, propionate, glycolat and oxalate are prepared calibrated for five different concentrations. The standard calibration curves are shown in the appendix I. The prepared standard solutions are stored in an HDPE vials container at 5 ˚C.

3.5.4.2 High Performance Liquid Chromatography (HPLC)

Samples obtained from the experimental run of the aqueous amine systems and to be analyzed using the High Performance Liquid Chromatography (HPLC) technique are termed analytes. This technique involves the use of a liquid phase, known as the mobile phase, to transport the liquid sample solution through a stationary phase. A stationary phase refers to a solid support, packed within a unit called column. The analyte is injected into the carrier mobile phase and it is forced to flow through the chromatographic stationary phase under a high pressure. As this flow takes place with the mobile phase and analyte through the stationary phase. The chemical interaction of the stationary phase and the sample with the mobile phase determines the degree of migration and separation of the components contained in the sample. This separation is thereafter reported as area percentages of peaks, representing quantitatively, the composition of the liquid sample. For a typical analysis, as much as 10.0 µL of sample was injected in order to ensure visualization of low-concentration products. The columns were kept at 30 ˚C. As stated, the HPLC technique uses a liquid mobile phase to transport the aqueous amine samples through the column. In this analysis, the mobile phase was a mixture of 0.02 mol/L KH_2PO_4 of pH 3.0 adjusted by 98% pure H_2SO_4. Ultra pure water (UPW) is used for the preparation of mobile phase and analytical standards. It was thereafter degassed in an ultrasonic water bath for 3 hours and filtered with a 0.2 µm nylon membrane filter before being used in the HPLC analysis. Prior to the analysis, samples were diluted to 1: 40 with ultra pure water (UPW), followed by filtration using a 0.20-µm nylon membrane filter. The errors of the HPLC were estimated to be less than ± 2%. The overall operating condition, column information and all parameters related to HPLC operation are given in Table 3.5.

Table 3.5: Operating condition and solvent of HP-LC (UV) method for identifying degraded alkanolamine samples

Parameters	**Details**	
Column Name	Supelco	
Column Dimensions	25.0 cm × 4.6 mm × ID 5.0 µm	
Stationary Phase	Supelcosil^{TM} LC-18	
Product Type	Protonated	
Mobile Phase	0.02 M KH_2PO_4 (Adjusted pH 3.0)	
Operating Temperature	25.0 ˚C	
Operating Pressure	80.0-100.0 MPa	Max. Pressure 500.0 MPa
Sample Type	Liquid	
Sample Preparation	Dilution Ratio: 1:40	Filter: 2.00 µm
Inject Volume	10.00 µl	
Wavelength Settled	214.00 µm	
Flow Rate	1.00 ml/min	
Analysis Time	35.00 min	
Detector	ELSD (Series 1200)	
Supplier	IT Tech Sdn. Bhd.	
Column Manufacturer	Agilent Technology, USA	
Flashing and Duration	UPW, 60.00 min	

3.5.4.3 Gas Chromatography Mass Spectrometer (GC-MS)

An HP-INNOWAX (length 30 m, internal diameter 0.250 mm, thickness 0.25 µm) packed with cross-linked polyethylene glycol was used in the GC-MS for the separation of components. These components were identified by their mass spectra. Prior to GC/MS analysis, each sample was diluted with ethanol to five times its original volume to avoid column overload and to improve separation of the components. An auto injector was used to automatically introduce samples into the GC column to give better reproducibility. Computer fitting of the mass spectrum to the mass spectra database was part of the strategy used to identify the samples. This was followed by the database of GCMS library in order to confirm the identification of the components in the samples. MS scan mode was used with a mass range from 10 to 300. The products were identified by matching their mass spectra with commercial mass spectra of the National Institute of Standards and Technology (NIST) database (1998 version). The samples were analyzed twice to check for reproducibility. A matching technique that compared the mass spectra of the GC-separated components with the NIST database was used for the initial product identification. Verification of some of the species was subsequently performed by comparing both the mass spectra and the GC retention time of commercially available pure standards with those of the initially identified components. However, after certain period of degradation reaction, a large number of degradation products are observed. The error of the GC/MS was estimated to be less than 3%. During analysis period a 10 µL syringe with an injection volume of 1.0 µL was used and a split mode was selected for the inlet with a split ratio of 30:1, split flow of 10.3 mL/min and total flow of 13.9 mL/min. The inlet temperature and pressure were 70°C and 9.18 psi, respectively. The initial temperature of the oven was 100°C with no holding time while the final temperature was 240 °C with a hold time of 10 min with an oven ramp of 10 °C/min for a total run time of 30 min.

The column flow rate was 0.5 mL/min while the pressure and average velocity were 9.18 psi and 37 cm/sec. For the MS parameters, the interface, quadruple and source temperatures were 250, 150 and 230 °C, respectively and the electron multiplier (EM) voltage was 1200 V. The overall operating conditions of GC/MS are summarized in the Table 3.6.

Table 3.6: Operating condition of GC-MS technique for analyzing CO_2 induced degradation of activated DEA and MDEA

Parameters	**Details**	
Column Name	HP-INNOWAX	
Column Dimensions	30.0 m × 0.250 mm × ID 0.25 µm	
Stationary Phase	HP-INNOWAX	
Column Type	High Polarity	
Mobile Phase	UHP He Gas	
Temperature	Initial 100.0 ˚C	Final 240.0 ˚C
Ramp Rate	7.0 ˚C	
Inlet temperature and pressure	Temperature 70.0 ˚C	Pressure 9.18 psi
EM Volt Temperature	250.0 ˚C, 150.0 ˚C, 230.0 ˚C	
EM Volt	1200.0 volt	
Sample Type	Liquid	
Sample Preparation	Dilution with UPW: 1:5	Filter: 2.00 µm
Inject Volume	1.00 µl	
Split Ratio	30:1	
Flow Rate	1.00 ml/min	
Analysis Time	25.00 min	
Detector	MSD	
Supplier	IT Tech Sdn. Bhd.	
Column Manufacturer	Agilent Technology, USA	

CHAPTER 04

RESULTS AND DISCUSSION

CHAPTER 04: RESULTS AND DISCUSSION

The characterization of degradation products of the five degradation systems for eighteen different samples were conducted using three different chromatographic methods, High Performance Liquid Chromatography-UV detection (HPLC-UV), Ion Chromatography (IC) and Gas Chromatography Mass Spectroscopy (GCMS). In this chapter degradation products of five degradation systems are discussed.

4.1 High Performance Liquid Chromatography (HPLC) Analysis with UV Detection

The initial trials were to evaluate the compatibility of the DB-WAX and Nucleosil columns with the mobile phases used for this study is potassium dihydrogen phosphate. Among these columns DB-WAX does not show sharp peaks during the analysis but the Nucleosil column showed sharp peaks. Based on result between two methods Nucleosil HPLC column and potassium dihydrogen phosphate mobile phase were selected for analysis. During the analysis two retention times was used for low and high concentration solution. The time was set to 25 and 35 minutes for low and high concentrated sample respectively. The unknown degradation products were identified based on standard verification by matching with specific retention time. There are fourty different standards including pure alkanlamines. For each individual standard solution concentration 5.00 ppm/Liter was prepared and retention time was noted, in this way forty standards are prepared and retention time noted for experimental analysis. Similarly the degraded reaction samples were diluted with UPW according to the same method and retention time was noted. The unknown degradation products were identified based on the retention time.

4.1.1 Degradation Products of PZ/H_2O/CO_2 System

The degradation products of PZ+H_2O+CO_2 system are summarized in the following Table 4.1 for two different concentrations of samples are DO1PZ1M and D02PZ2M at 100 ˚C. Figures 4.1 (a, b) and 4.2 illustrate the chromatograms of D01PZ1M and DO2PZ2M samples respectively.

4.1.1.1 Degradation Products of D01PZ1M Sample

The sample D01PZ1M constits of 1M carbonated aqueous piperazine. There are five peaks observed in the chromatogram where as two peaks are identified. Peak number three is formamide and peak number five is 2-(2-aminoethoxy)-ethanol, it is also called diglycolamine (DGA). Freeman et al. in 2009 studied the degradation behavior of PZ induced by gas mixture (CO_2+O_2) and found formamide as a degradation product. Sexton conducted an experiment on the degradation behavior of PZ by a mixture of two gases CO_2 and O_2 and found formamide as degradation products too (Sexton, 2008).

The same sample D01PZ1M is analyzed two times. First time it was analyzed for twenty minutes and second time it was analyzed for thirty five minutes. There are eight peaks were found in the chromatogram, however only three peaks were identified. One additional DGP is detected in this method which is 2-methoxyethanol (peak number five). Other two identified DGPs are similar with the identified DGPs found in the figure 4.1a. The identified degradation products are formamide, 2-methoxyethanol and 2-(2-aminoethoxy) ethanol.

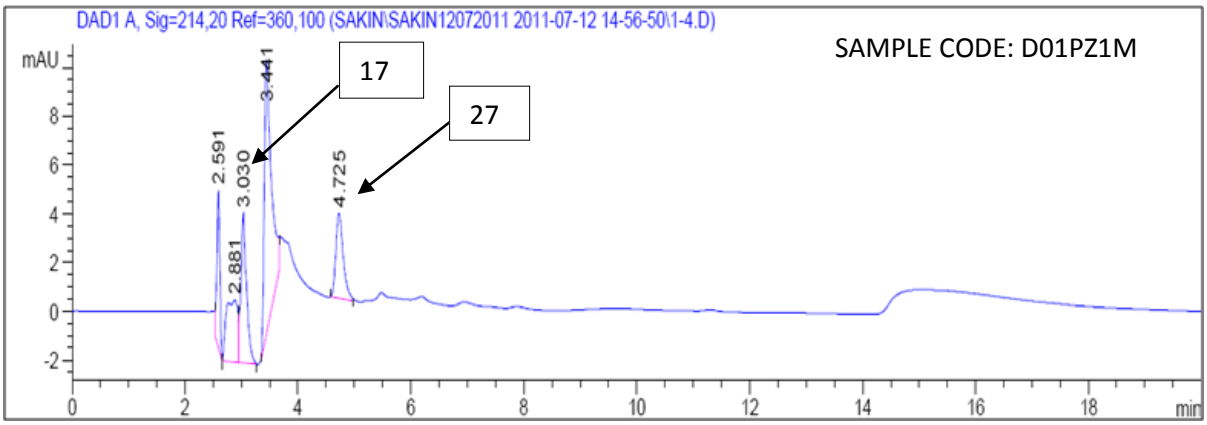


Figure 4.1a: Chromatograms of carbon dioxide induced degradation of D01PZ1M identified by HPLC-UV method.

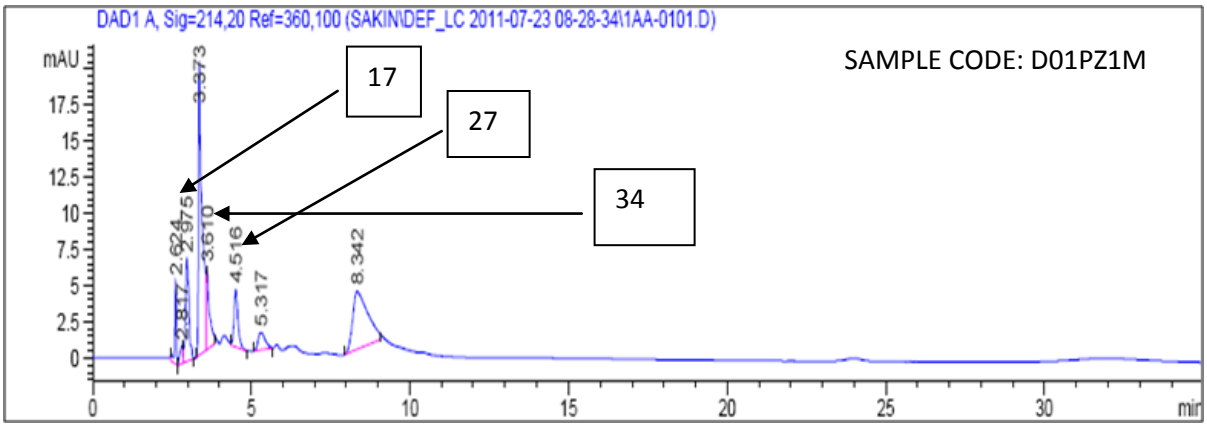


Figure 4.1b: Chromatograms of carbon dioxide induced degradation of D01PZ1M identified by HPLC-UV method.

Table 4.1: List of carbon dioxide induced degradation products of D01PZ1M identified by HPLC-UV method

DS: PZ+H_2O+CO_2, Temperature: 100 ˚C, Pressure: 1.00 atm, [PZ]: 1M, Identification Method: HPLC-UV, L_α:0.4, R_α:0.6									
Sample Code	**Peak No**	**Observed RT of Peak**	**Peak Level**	**Peak Area (%)**	**RT of Standard**	**Standard Verification**	**M. Formula**	**M. Weight**	**Identity**
DO1PZ1M (Fig. 4.1a)	1	2.591	51	10.239	2.601	Detected	H_2O	18.00	Water
	2	2.881	-	15.466	-	X	-	-	UN
	3	3.030	17	18.616	2.996	Detected	$HCONH_2$	45.04	Formamide
	4	3.441	-	41.853	-	X	-	-	UN
	5	4.725	27	13.823	4.77	Detected	$C_4H_{11}NO_2$	105.14	2-(2-aminoethoxy)ethanol
DO1PZ1M (Fig. 4.1b)	1	2.624	51	4.544	2.601	Detected	H_2O	18.00	Water
	2	2.817	-	1.869	-	X	-	-	UN
	3	2.975	17	11.818	2.996	Detected	$HCONH_2$	45.04	Formamide
	4	3.373	-	33.648	-	X	-	-	UN
	5	3.610	34	8.567	3.745	Detected	$C_3H_8O_2$	76.09	2-Methoxyethanol
	6	4.516	27	7.289	4.77	Detected	$C_4H_{11}NO_2$	105.14	2-(2-aminoethoxy)ethanol
	7	5.317	-	4.016	-	X	-	-	UN
	8	8.342	-	28.246	-	X	-	-	UN

N.B: UN-Unknown, RT-Retention Time (Min), X- Does Not Match

4.1.1.2 Degradation Products of D02PZ2M Sample

The chromatogram of this sample is shown in the figure 4.2. There are five peaks observed in the chromatogram, number one is for water with peak level is 51. Peaks number three and six are detected and they are formamied and 2-methoxyethanol respectively. Sexton and Freeman studied the degradation behavior of PZ and found formamide as a degradation product (Freeman, 2010; Sexton, 2008). Amines are easily oxidized and converted into alcohol and further react with other chemical species. 2-methoxy ethanol could be a new DGP. Carttee and his coworkers showed a ring opening reaction mechanism of cyclic amine where as explained that piperazine is a cyclic diamine which is capable to produce alcohol or secondary products by degradation reaction (Lepaumier et al., 2009c, b; Lepaumier et al., 2010,).

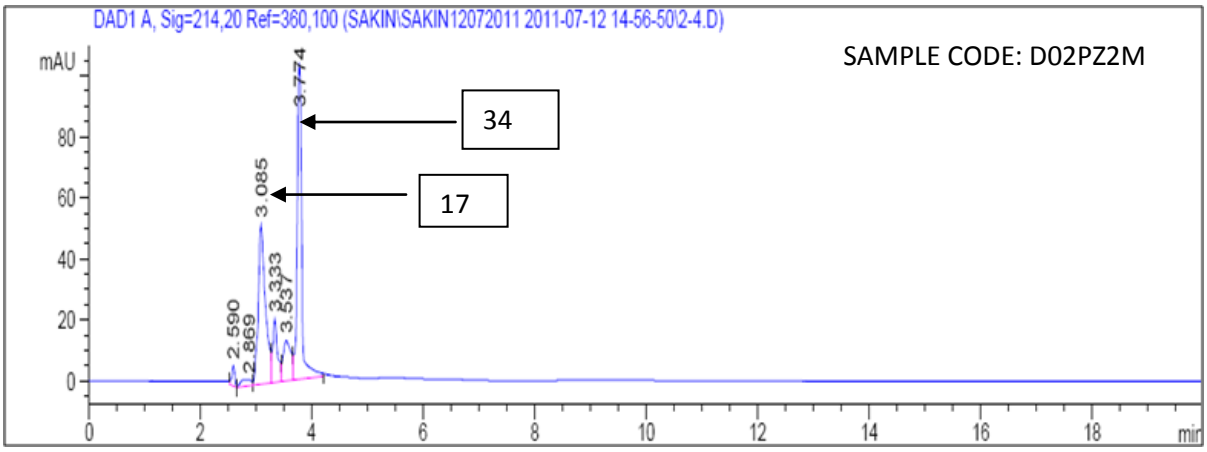


Figure 4.2: Chromatograms of carbon dioxide induced degradation of D02PZ2M identified by HPLC-UV method.

Table 4.2: List of carbon dioxide induced degradation products D02PZ2M identified by HPLC-UV method

DS: PZ+H_2O+CO_2, Temperature: 100 ˚C, Pressure: 1.00 atm, L_α:0.3, R_α:0.8, [PZ]: 2M, Identification method: HPLC-UV									
Sample Code	**Peak No**	**Observed RT of Peak**	**Peak Level**	**Peak Area (%)**	**RT of Standard**	**Standard Verification**	**M. Formula**	**M. Weight**	**Identity**
DO2PZ2M (Fig. 5.2)	1	2.590	51	1.685	2.601	Detected	H_2O	18.00	Water
	2	2.869	-	2.012	-	X	-	-	UN
	3	3.085	17	34.085	2.996	Detected	$HCONH_2$	45.04	Formamide
	4	3.33	-	9.061	-	X	-	-	UN
	5	3.537	-	9.693	-	X	-	-	UN
	6	3.774	34	43.463	3.745	Detected	$C_3H_8O_2$	76.09	2-Methoxyethanol

N.B: UN-Unknown, RT-Retention Time (Min), X- Does Not Match

4.1.1.3 Variation of Peak Areas of Degradation Products (DGPs) of PZ+H_2O+CO_2 System

The peak area is the integration of the mass per unit volume (concentration) of eluted solute eluted with respect to time. Peak areas can be measured manually it is obtained as the product of the peak height and the peak width. Figure 4.3 represents the variation of peak areas of each degradation products of D01PZ1M and D02PZ2M. The main degradation products of D01PZ1M are found Formamide (FM) and 2-(2-aminoethoxy)ethanol (AEE) which are indicated in the bar diagram. On the other hand for D02PZ2M, the degradation products are identified Formamide (FM) and 2-Methoxyethanol (MOE). The unidentified peak areas of DGPs for D01PZ1M and D02PZ2M are not indicated in the figure. From the figure it was found that the concentration of Formamide is increasing with amine concentration and the highest concentration of DGPs for D02PZ2M is MOE.

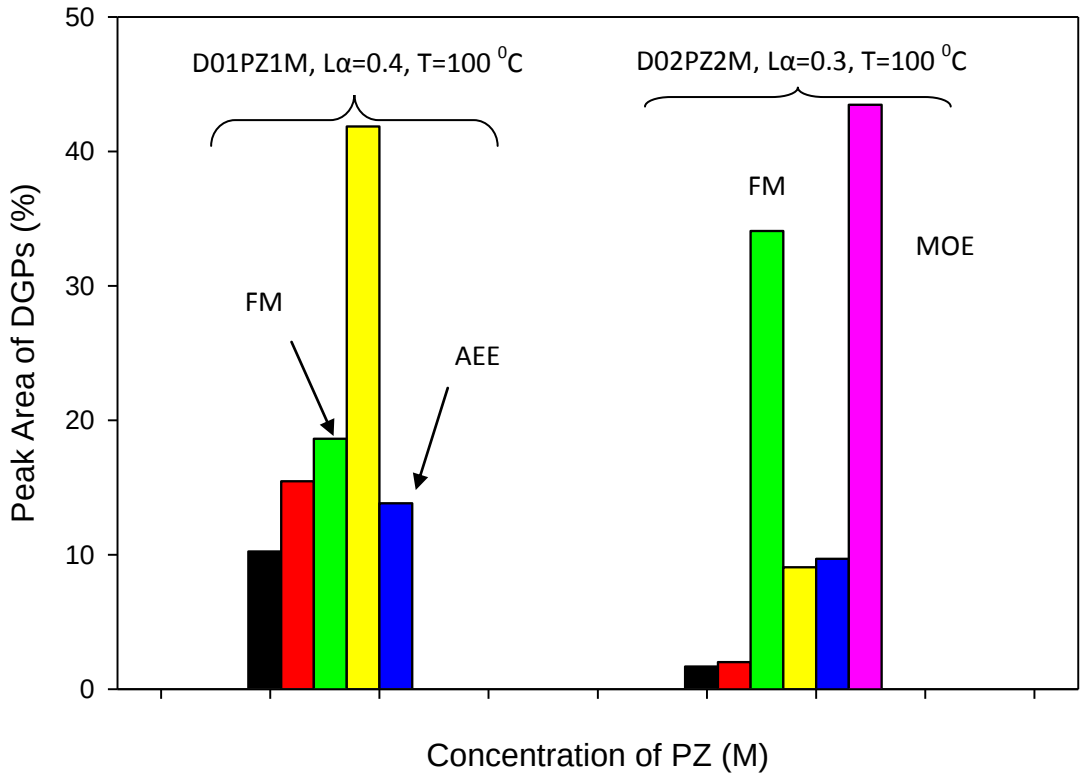


Figure 4.3: Variation of Degradation Products of D01PZ1M and D02PZ2M

4.1.2 Degradation Products of DEA/H_2O/CO_2 System

Three different degraded solutions of this system are D03DEA2M, D04DEA3M and D05DEA4M were analyzed and the obtained DGPs are discussed in the following section.

4.1.2.1 Degradation Products of D03DEA2M Sample

The chromatogram shown in figure 4.4 represents twelve observed peaks. Nine peaks are identified and three of these are not detected. Among these nine peaks seven are treated as DGPs these are formamide, 2-methoxyethanol, diethylenetriamine, 2-(2-aminoethoxy) ethanol, triethanolamine, acetone and ethyl 1-piperazinecarboxylate. The results are summarized in table 4.3. None of the polymeric degradation products were detected. Diethanolamine is generally degraded into monoethanolamine (Dawodu and Meisen, 1991) and both amines are capable to produce acids and alcohol (M. S.Islam, 2010). Later acid and alcohol produced acetate and aldehyde and ketone. Supap and his co-workers (2006) conducted an experiment on the degradation of MEA induced by carbon dioxide and reported that acetone, ethanol, acetate and amides were identified by HPLC and GC-MS (Supap et al., 2006).

Triethanolamine is a degradation product of DEA reported by Dawodu and Meisen in 1991. Dawodu and Meisen separately conducted the degradation study of DEA induced by COS and CO_2 in both cases they identified HEP, BHEP and TEA (Dawodu and Axel Meisen, 1994; Dawodu and Meisen, 1991). Etylaminoethanol (EAE) is a derivative of ethanol, it is identified by Dawodu and Meisen (Dawodu and Meisen, 1991). HEP and BHEP are the byproducts of piperazine identified in the degradation of DEA, it can be argued that DEA easily converts to PZ and it has the capability to produce further by products.

In this work Ethyl 1-piperazinecarboxylate is identified which is a derivative of PZ. Diethylenetriamine is derivative of TEA and the two ethanol derivatives are 2-(2-aminoethoxy) ethanol and 2-Methoxyethanol are also identified. Molecular weight, peak area, retention time and peak level of all identified DGPs are summarized in table 4.3.

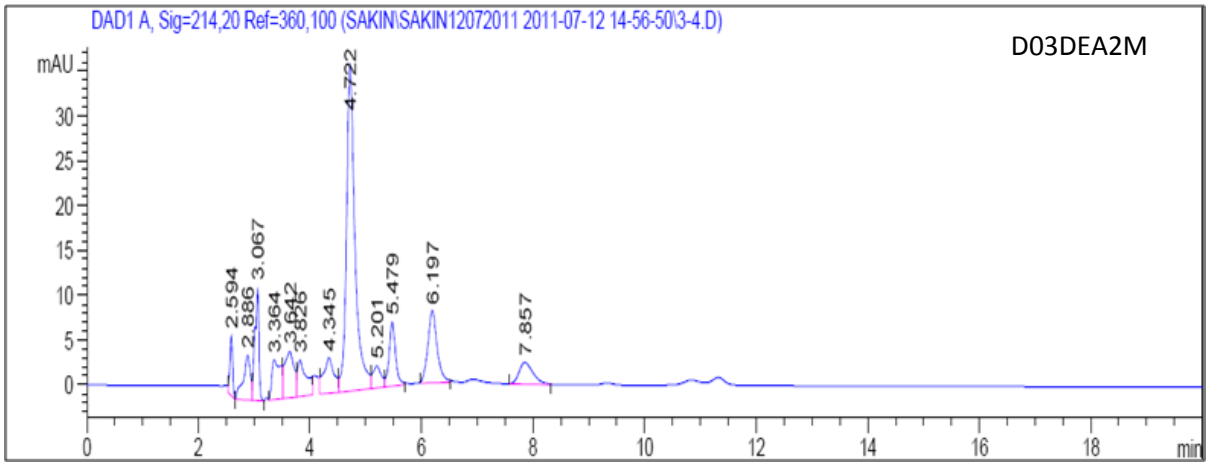


Figure 4.4: Chromatograms of carbon dioxide induced degradation of D03DEA2M identified by HPLC-UV.

Table 4.3: List of carbon dioxide induced degradation products of D03DEA2M identified by HPLC-UV method

DS: DEA+H_2O+CO_2, T-100 ˚C, P-1.00 atm, L_α: 0.28 R_α: 0.58, [DEA]: 2M, Identification Method: HPLC (UV)									
Sample Code	**Peak No**	**Observed RT of Peck**	**Peak Level**	**Peak Area (%)**	**RT of Standard**	**Standard Verification**	**M. Formula**	**M. Weight**	**Identity**
DO3DEA2M	1	2.594	51	2.472	2.601	Detected	H_2O	18.00	Water
	2	2.886	17	4.645	2.996	Detected	$HCONH_2$	45.04	Formamide
	3	3.067	17	6.777	2.996	Detected	$HCONH_2$	45.04	Formamide
	4	3.364	-	4.943	-	X	-	-	UN
	5	3.642	-	6.489	-	X	-	-	UN
	6	3.826	34	5.053	3.745	Detected	$C_3H_8O_2$	76.09	2-Methoxyethanol
	7	4.345	11	5.618	4.279	Detected	$C_4H_{13}N_3$	103.17	Diethylenetriamine
	8	4.722	27	40.828	4.772	Detected	$C_4H_{11}NO_2$	105.14	2-(2-aminoethoxy)ethanol
	9	5.201	26	2.673	5.040	Detected	$C_6H_{15}NO_3$	149.19	Triethanolamine (TEA)
	10	5.479	-	6.072	-	X	-	-	UN
	11	6.197	45	9.905	6.092	Detected	C_3H_6O	58.08	Acetone
	12	7.857	15	4.521	7.776	Detected	$C_7H_{14}N_2O_2$	158.20	Ethyl 1-piperazinecarboxylate

N.B: UN-Unknown, RT-Retention Time (Min), X- Does Not Match

4.1.2.2 Degradation Products of D04DEA3M Sample

Diethanolamine (DEA) sample with code number D04DEA3M where as the amine concentration is 3M was degraded under experimental condition and analyzed by HPLC-UV method. The chromatogram shown in figure 4.5 which reveals fourteen peaks of different DGPs. Nine peaks are identified and the rest are not detected. The detected degradation products are formamide, 2-methoxyethanol, diethylenetriamine, 2-(2-aminoethoxy) ethanol, triethanolamine, acetone and ethyl 1-piperazinecarboxylate. The results are summarized in table 4.4. No polymeric degradation products were detected. Supap and his co-workers in 2006 conducted CO_2 induced degradation of MEA and reported that acetone, ethanol, acetate and amides are DGP. Dawodu and Meisen separately conducted the degradation study of DEA induced by COS and CO_2 in both cases they identified HEP, BHEP and TEA as degradation products (Dawodu and Axel Meisen, 1994; Dawodu and Meisen, 1991). Etylaminoethanol (EAE) is a derivative of ethanol, it is identified by Dawodu and Meisen in the above studies too (Dawodu and Meisen, 1991). HEP and BHEP are the byproducts of piperazine identify in the degradation of DEA, in this point of view it can be said that DEA easily converted to PZ and it has the capability to produce further by products. In this work Ethyl 1-piperazinecarboxylate is identified this is also derivative of PZ. Diethylenetriamine this is a derivative of TEA and two ethanol derivatives are 2-(2-aminoethoxy) ethanol, 2-Methoxyethanol were found in this work. Peak number one is for water this is not a degradation products as identified for the presence of process water in sample. The result is also reported by several researchers previously (Dawodu and Meisen, 1996, 1991; M. S.Islam, 2010).

Basically the degradation products of D04DEA3M are same with D03DEA2M sample, but D04DEA3M shows few additional peaks which are not detected. In between these two compounds it was found that higher concentrated DEA degraded more according to the visible peaks into the chromatogram. The possible reasons for the formation of these degradation products are already discussed in the above description. However, among the identified DGPs, 2-(2-aminoethoxy)-ethanol was found grater concentration than all and formamide was second highest concentration. Low concentrated DGPs are diethylenetriamine, acetone, TEA and ethyl-1-piperazie- carboxylate which are derivative of amine and acids. TEA is identified in this system, it was predicted that DEA degraded and once it is converted into TEA.

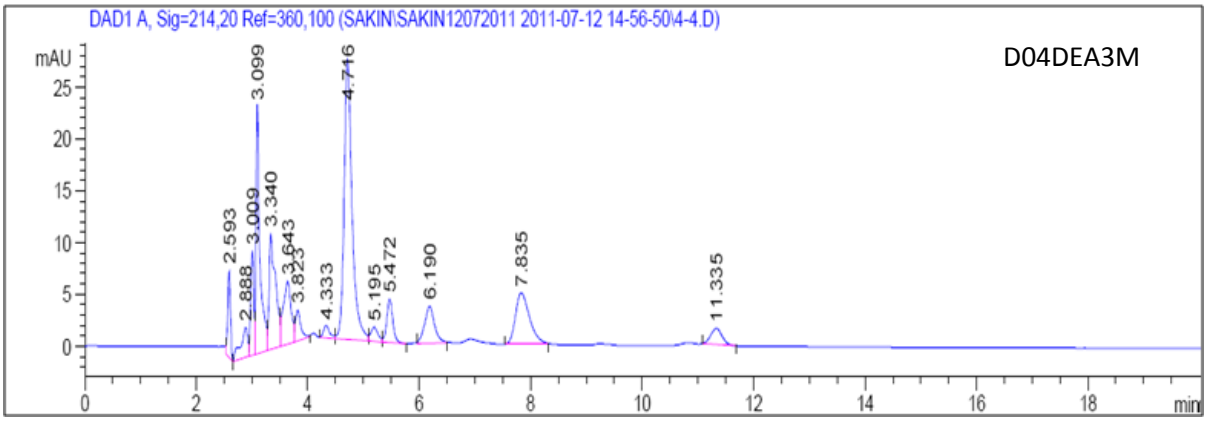


Figure 4.5: Chromatograms of carbon dioxide induced degradation of D04DEA3M identified by HPLC-UV method.

Table 4.4: List of carbon dioxide induced degradation products of D04DEA3M identified by HPLC-UV method

System: DEA+H_2O+CO_2, T-100 ˚C, P-1.00 atm, L_α: 0.27, R_α: 0.56, [DEA]: 3M, Identification Method: HPLC (UV)									
Sample Code	**Peak No**	**Observed RT of Peck**	**Peak Level**	**Peak Area (%)**	**RT of Standard**	**Standard Verification**	**M. Formula**	**M. Weight**	**Identity**
DO4DEA3M	1	2.593	51	3.320	2.601	Detected	H_2O	18.00	Water
	2	2.888	-	2.980	-	X	-	-	UN
	3	3.009	17	4.599	2.996	Detected	$HCONH_2$	45.04	Formamide
	4	3.099	17	13.685	2.996	Detected	$HCONH_2$	45.04	Formamide
	5	3.340	-	10.552	-	X	-	-	UN
	6	3.643	34	6.871	3.745	Detected	$C_3H_8O_2$	76.09	2-Methoxyethanol
	7	3.823	-	2.417	-	X	-	-	UN
	8	4.333	11	1.106	4.279	Detected	$C_4H_{13}N_3$	103.17	Diethylenetriamine
	9	4.716	27	31.207	4.772	Detected	$C_4H_{11}NO_2$	105.14	2-(2-aminoethoxy)ethanol
	10	5.195	26	1.482	5.040	Detected	$C_6H_{15}NO_3$	149.19	Triethanolamine (TEA)
	11	5.472	-	3.699	-	X	-	-	UN
	12	6.190	45	5.143	6.092	Detected	C_3H_6O	58.08	Acetone
	13	7.835	15	10.332	7.776	Detected	$C_7H_{14}N_2O_2$	158.20	Ethyl 1-piperazinecarboxylate
	14	11.335	-	2.600	-	X	-	-	UN

N.B: UN-Unknown, RT-Retention Time (Min), X- Does Not Match

4.1.2.3 Degradation Products of D05DEA4M Sample

The chromatogram of sample is presented in figure 4.6, it consists of fifteen peaks of different DGPs, nine peaks are identified. Peak number fifteen of RT 10.802 is identified wich is the same observed in figure 4.5 as RT 11.335. The detected degradation products are diethylenetriamine, ethyl-1-piperazinecarboxylate, formamide, triethanolamine, 2-(2-aminoethoxy) ethanol, 2-methoxyethanol, ethanol and acetone and are summarized in the Table 4.5.

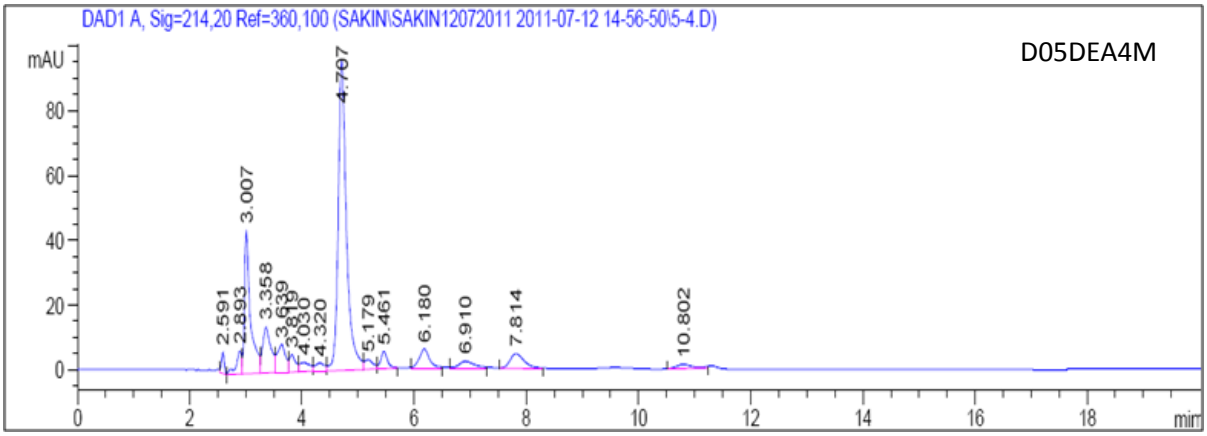


Figure 4.6: Chromatograms of carbon dioxide induced degradation of D05DEA4M identified by HPLC-UV method.

Table 4.5: List of carbon dioxide induced degradation products of D05DEA4M identified by HPLC-UV method

DS: DEA+H_2O+CO_2, T-100 ˚C, P-1.00 atm, L_α: 0.34, R_α: 0.59, [DEA]: 4M, Method: HPLC (UV)									
Sample Code	**Peak No**	**Observed RT of Peck**	**Peak Level**	**Peak Area (%)**	**RT of Standard**	**Standard Verification**	**M. Formula**	**M. Weight**	**Identity**
DO5DEA4M	1	2.591	51	1.101	2.601	Detected	H_2O	18.00	Water
	2	2.893	-	2.357	-	X	-	-	UN
	3	3.007	17	16.149	2.996	Detected	$HCONH_2$	45.04	Formamide
	4	3.358	-	7.276	-	X	-	-	UN
	5	3.639	-	4.450	-	X	-	-	UN
	6	3.819	34	2.164	3.745	Detected	$C_3H_8O_2$	76.09	2-Methoxyethanol
	7	4.030	46	1.792	4.117	Detected	C_2H_6O	-	Ethanol
	8	4.320	25	1.435	4.437	Detected	$C_4H_{11}NO_2$	105.14	Diethanolamine (DEA)
	8	4.320	11	1.435	4.279	Detected	$C_4H_{13}N_3$	103.17	Diethylenetriamine
	9	4.707	27	48.646	4.772	Detected	$C_4H_{11}NO_2$	105.14	2-(2-aminoethoxy)ethanol
	10	5.179	12	1.563	5.119	Detected	$C_4H_{12}N_2O$	104.15	N-(2-Hydroxyethyl)ethylenediamine (HEED)
	11	5.461	-	2.287	-	X	-	-	UN
	12	6.180	45	3.652	6.092	Detected	C_3H_6O	58.08	Acetone
	13	6.910	-	1.881	-	X	-	-	UN
	14	7.814	15	3.919	7.776	Detected	$C_7H_{14}N_2O_2$	158.20	Ethyl-1-piperazinecarboxylate
	15	10.802	-	1.321	-	X	-	-	UN

N.B: UN-Unknown, RT-Retention Time (Min), X- Does Not Match

4.1.2.4 Variation of Peak Areas of Identified DGPs of DEA+H_2O+CO_2 System

Figure 4.7 represents the variation of peak areas of identified DGPs of D03DEA2M, D04DEA3M and D05DEA4M. The major DGPs of D03DEA2M, D04DEA3M and D05DEA4M are formamide (FM), 2-Methoxyethanol (MOE), 2-(2-aminoethoxy)ethanol (AEE), acetone (AC) and Ethyl-1-piperazinecarboxylate (EPC). The numbers of DGPs are increases with amine concentration and 2-(2-aminoethoxy)-ethanol posses heighest peak areas among all DGPs. The peak areas of FM are also increases with alkanolamine concentration. The others DGP are posses relatively low peak ares which are not indicated in the following figure. Therefore it was clearly appeared in the figure that the peak areas of DGPs are changed randomly except FM.

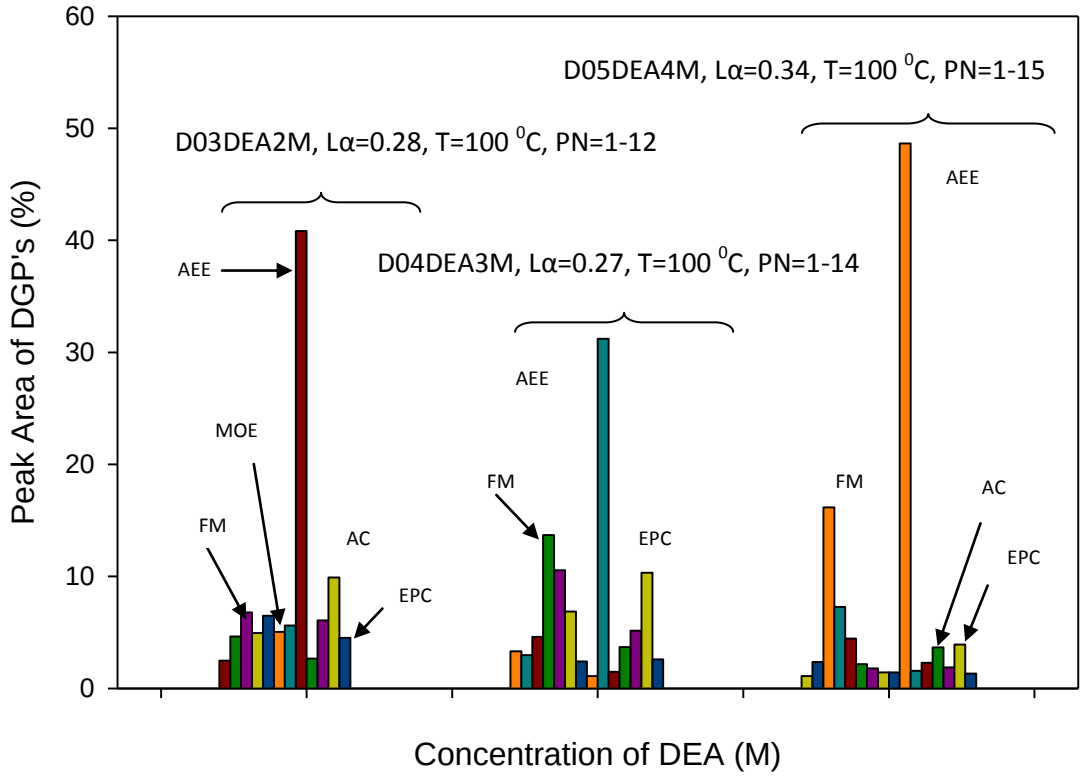


Figure 4.7: Variation of Peak Areas of Identified DGPs of D03DEA2M, D04DEA3M and D05DEA4M

4.1.3 Degradation Products of DEA+PZ+H_2O+CO_2 System

Five degraded samples D06DEA2MPZ1M, D07DEA2MPZ2M, D08DEA3MPZ2M, D09DEA4MPZ2M and D10DEA7MPZ2M of this degradation system were analyzed and the results are discussed in the following section.

4.1.3.1 Degradation Products of D06DEA2MPZ1M

The activated aqueous solution of diethanolamine (DEA) with code number D06DEA2MPZ1M consists of 2M diethanolamine (DEA) and 1M piperazine (PZ). The degradation of DEA blends with PZ is illustrated in figure 4.8. The chromatogram shows eleven peaks of different DGPs. Seven peaks are detected these are formamide, 2-methoxyethanol, diethylenetriamine, 2-(2-aminoethoxy) ethanol and ethyl 1-piperazinecarboxylate. Identified degradation products are five summarized in table 4.6 with details information about peak area, peak level, molecular formula, molecular weight and identity. Based on the available degradation results of 2M diethanolamine and activated DEA solutions, activated DEA is more resistant to degradation even though numbers of identified degradation products are lower than inactivated one.

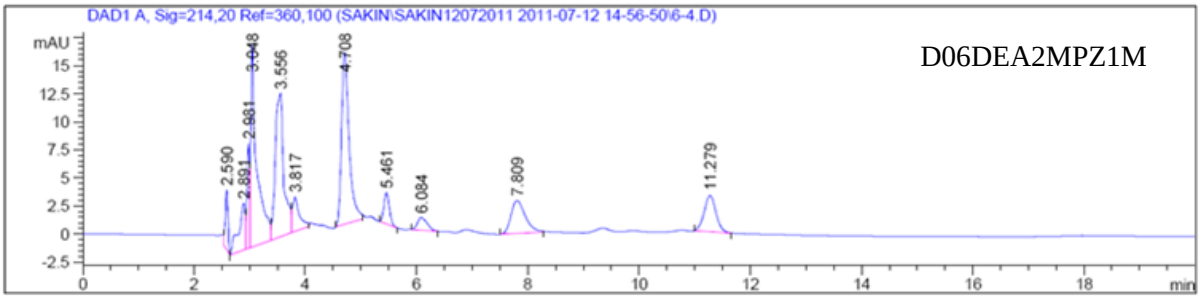


Figure 4.8: Chromatograms of carbon dioxide induced degradation of D06DEA2MPZ1M identified by HPLC-UV method.

Table 4.6: List of carbon dioxide induced degradation products of D06DEA2MPZ1M identified by HPLC-UV method

System: DEA+PZ+H_2O+CO_2, T-100 ˚C, P-1.00 atm, L_α: 0.40, R_α: 0.70, [DEA/PZ]: 2/1, Method: HPLC (UV)									
Sample Code	**Peak No**	**Observed RT of Peck**	**Peak Level**	**Peak Area (%)**	**RT of Standard**	**Standard Verification**	**M. Formula**	**M. Weight**	**Identity**
D06DEA2MPZ1M (Fig. 4.8)	1	2.590	51	2.818	2.601	Detected	H_2O	18.00	Water
	2	2.891	-	5.066	-	X	-	-	UN
	3	2.981	17	4.807	2.996	Detected	$HCONH_2$	45.04	Formamide
	4	3.048	17	20.475	2.996	Detected	$HCONH_2$	45.04	Formamide
	5	3.556	-	20.697	--	X	-	-	UN
	6	3.817	34	4.155	3.745	Detected	$C_3H_8O_2$	76.09	2-Methoxyethanol
	7	4.708	27	21.738	4.772	Detected	$C_4H_{11}NO_2$	105.14	2-(2-aminoethoxy)ethanol
	8	5.461	-	2.867	-	X	-		UN
	9	6.084	45	2.085	6.092	Detected	C_3H_6O	58.08	Acetone
	10	7.809	15	8.036	7.776	Detected	$C_7H_{14}N_2O_2$	158.20	Ethyl 1-piperazinecarboxylate
	11	11.279	-	7.251	-	X	-	-	UN

N.B: UN-Unknown, RT-Retention Time (Min), X- Does Not Match

4.1.3.2 Degradation Products of D07DEA2MPZ2M

Degraded diethanolamine (DEA) with code number D07DEA2MPZ2M consists of 2M diethanolamine and 2M piperazine. In order to investigate degradation phenomenon of this sample it was analyzed and observed chromatogram shown in figure 4.9. In this chromatogram seven peaks of different DGPs are identified and five are detected. Detected degradation products are formamide, 2-methoxyethanol, 2-(2-aminoethoxy) ethanol, and ethyl-1-piperazinecarboxylate are summarized in table 4.7 with details information about peak area, peak level, molecular formula, molecular weight and identity. Based on the results of this sample D07DEA2MPZ2M, it is showed better resistance over all inactivated DEA samples D03DEA2M, D04DEA3M and D05DEA4M even though number of degradation products are lower than activated sample D06DEA2MPZ1M.

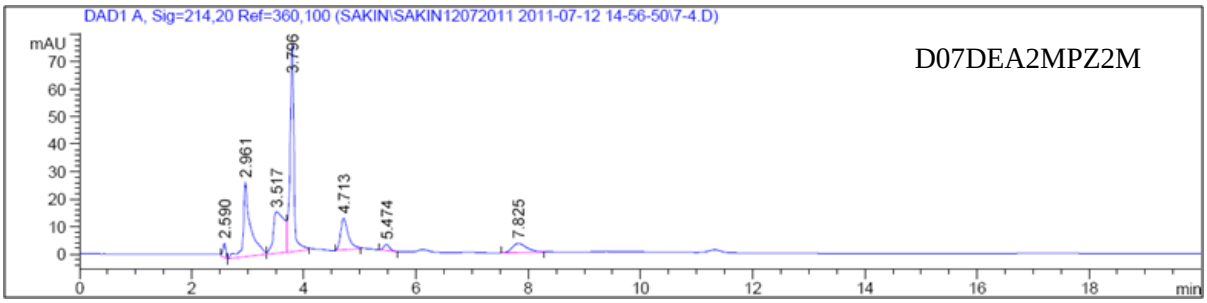


Figure 4.9: Chromatograms of carbon dioxide induced degradation of D07DEA2MPZ2M identified by HPLC-UV method.

Table 4.7: List of carbon dioxide induced degradation products of D07DEA2MPZ2M identified by HPLC-UV method

DS: DEA+PZ+H_2O+CO_2, T-100 ˚C, P-1.00 atm, L_α: 0.30, R_α: 0.70, [DEA/PZ]: 2/2, Method: HPLC (UV)									
Sample Code	**Peak No**	**Observed RT of Peck**	**Peak Level**	**Peak Area (%)**	**RT of Standard**	**Standard Verification**	**M. Formula**	**M. Weight**	**Identity**
D07DEA2MPZ2M	1	2.590	51	1.729	2.601	Detected	H_2O	18.00	Water
	2	2.961	17	23.679	2.996	Detected	$HCONH_2$	45.04	Formamide
	3	3.517		19.677	-	X	-	-	UN
	4	3.796	34	36.718	3.745	Detected	$C_3H_8O_2$	76.09	2-Methoxyethanol
	5	4.713	27	10.649	4.772	Detected	$C_4H_{11}NO_2$	105.14	2-(2-aminoethoxy)ethanol
	6	5.474		1.525	-	X	-	-	UN
	7	7.825	15	6.020	7.776	Detected	$C_7H_{14}N_2O_2$	158.20	Ethyl 1-piperazinecarboxylate

N.B: UN-Unknown, RT-Retention Time (Min), X- Does Not Match

4.1.3.3 Degradation Products of D08DEA3MPZ2M

Degraded D08DEA3MPZ2M sample consists of 3M Diethanolamine and 2M piperazine is analyzed and figure 4.10 shows the chromatogram of DGPs. In this chromatogram ten peaks of different DGPs were observed and five are detected. Identified degradation products are formamide, 2-methoxyethanol, 2-(2-aminoethoxy) ethanol, and ethyl-1-piperazinecarboxylate are summarized in table 4.8 with details information about peak area, peak level, molecular formula, molecular weight and identity. Based on the results of the sample shows shows better resistance to degradation over all inactivated DEA samples D03DEA2M, D04DEA3M and D05DEA4M even though numbers of degradation products are lower than activated sample D06DEA2MPZ1M

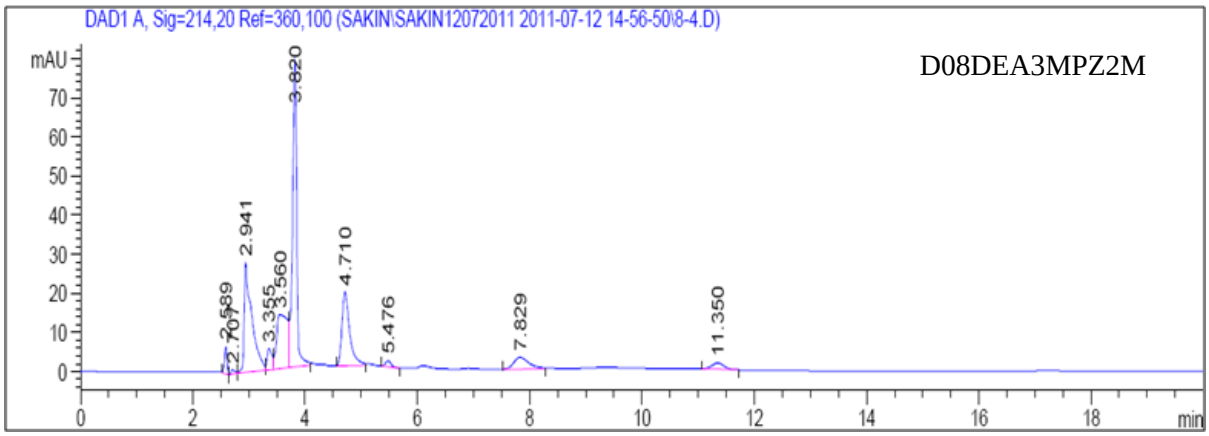


Figure 4.10: Chromatograms of carbon dioxide induced degradation of D08DEA3MPZ2M identified by HPLC-UV method.

.

Table 4.8: List of carbon dioxide induced degradation products of D08DEA3MPZ2M identified by HPLC-UV method

DS: DEA+PZ+H_2O+CO_2, T-100 °C, P-1.00 atm, L_α: 0.32, R_α: 0.72, [DEA/PZ]: 3/2, Method: HPLC (UV)									
Sample Code	**Peak No**	**Observed RT of Peck**	**Peak Level**	**Peak Area (%)**	**RT of Standard**	**Standard Verification**	**M. Formula**	**M. Weight**	**Identity**
D08DEA3MPZ2M	1	2.589	51	1.834	2.601	Detected	H_2O	18.00	Water
	2	2.707	-	0.470	-	X	-	-	UN
	3	2.941	17	22.199	2.996	Detected	$HCONH_2$	45.04	Formamide
	4	3.355	-	2.758	-	X	-	-	UN
	5	3.560	-	15.433	--	X	-	-	UN
	6	3.820	34	34.865	3.745	Detected	$C_3H_8O_2$	76.09	2-Methoxyethanol
	7	4.710	27	14.853	4.772	Detected	$C_4H_{11}NO_2$	105.14	2-(2-aminoethoxy)ethanol
	8	5.476	-	0.902	-	X	-	-	UN
	9	7.829	15	4.611	7.776	Detected	$C_7H_{14}N_2O_2$	158.20	Ethyl 1-piperazinecarboxylate
	10	11.350	-	2.072	-	X	-	-	UN

N.B: UN-Unknown, RT-Retention Time (Min), X- Does Not Match

4.1.3.4 Degradation Products of D09DEA4MPZ2M

This degraded sample D09DEA4MPZ2M consists of 4M diethanolamine and 2M piperazine is analyzed in order to investigate degradation products. Figure 4.11 shows chromatogram for fourteen peaks of different DGP and seven peaks are detected. Among these detected seven peaks six are identified as degradation products these are formamide, 2-methoxyethanol, 2-(2-aminoethoxy) ethanol, 1-(2-Aminoethyl) piperazine, 1,4-dimethylpiperazine and ethyl-1-piperazinecarboxylate summarized in Table 4.9.

Two additional DGPs 1-(2-aminoethyl)-piperazine and 1, 4-dimethylpiperazine are found. Contrary to the other samples such as D06DEA2MPZ1M, D07DEA2MPZ2M and D08DEA3MPZ2M they does not show these two DGPs. Based on the results it is showed better resistance over all inactivated DEA samples D03DEA2M, D04DEA3M and D05DEA4M. By considering the number of degradation products it could be argued that D09DEA4MPZ2M degraded more by comparing with activated D06DEA2MPZ1M, D07DEA2MPZ2M and D08DEA3MPZ2M.

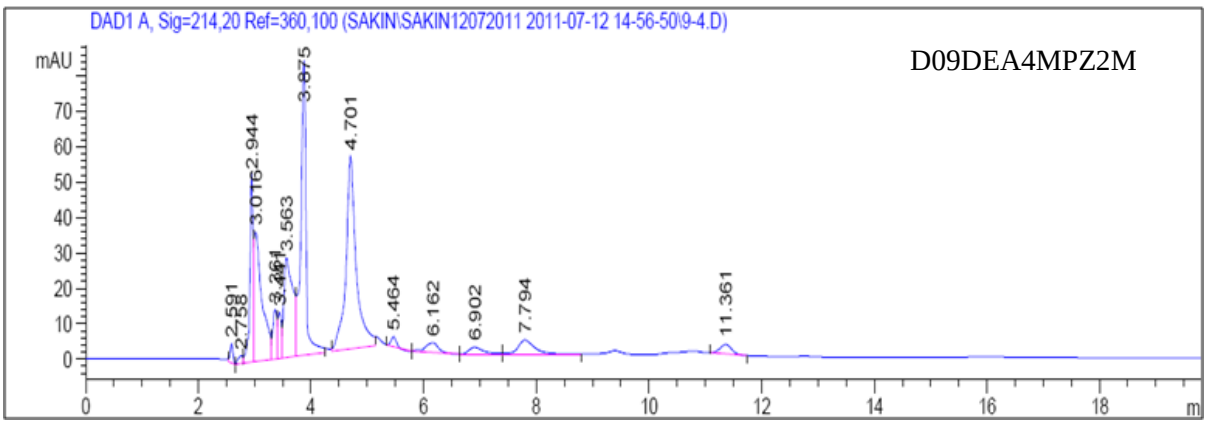


Figure 4.11: Chromatograms of carbon dioxide induced degradation of D09DEA4MPZ2M identified by HPLC-UV method.

Table 4.9: List of carbon dioxide induced degradation products of D09DEA4MPZ2M identified by HPLC-UV method

DS: DEA+PZ+H_2O+CO_2, T-100 ˚C, P-1.00 atm, L_α: 0.30, R_α: 0.71, [DEA/PZ]: 4/2, Method: HPLC (UV)									
Sample Code	**Peak No**	**Observed RT of Peck**	**Peak Level**	**Peak Area (%)**	**RT of Standard**	**Standard Verification**	**M. Formula**	**M. Weight**	**Identity**
DO9DEA4MPZ2M	1	2.591	51	0.748	2.601	Detected	H_2O	18.00	Water
	2	2.758	-	0.502	-	X	-	-	UN
	3	2.944	-	8.858	-	X	-	-	UN
	4	3.016	17	14.195	2.996	Detected	$HCONH_2$	45.04	Formamide
	5	3.361	-	2.933	-	X	-	-	UN
	6	3.441	-	2.116	-	X	-	-	UN
	7	3.563	-	12.498	-	X	-	-	UN
	8	3.875	34	21.963	3.745	Detected	$C_3H_8O_2$	76.09	2-Methoxyethanol
	9	4.701	27	27.625	4.772	Detected	$C_4H_{11}NO_2$	105.14	2-(2-aminoethoxy)ethanol
	10	5.464	4	0.552	5.638	Detected	$C_6H_{15}N_3$	129.20	1-(2-Aminoethyl) piperazine
	11	6.162	-	1.774	-	X	-	-	UN
	12	6.902	18	1.457	6.754	Detected	$C_6H_{14}N_2$	114.19	1,4-Dimethylpiperazine
	13	7.794	15	3.220	7.776	Detected	$C_7H_{14}N_2O_2$	158.20	Ethyl 1-piperazinecarboxylate
	14	11.361	-	1.554	-	X	-	-	UN

N.B: UN-Unknown, RT-Retention Time (Min), X- Does Not Match

4.1.3.5 Degradation Products of D10DEA7MPZ2M

D10DEA7MPZ2M consists of 7M diethanolamine and 2M. Figure 4.12 shows the chromatogram for eighteen peaks of different DGPs including water but seven peaks are detected. Identified degradation products are formamide, 2-methoxyethanol, 2-(2-aminoethoxy) ethanol, 1-(2-Aminoethyl) piperazine, 1, 4-dimethylpiperazine and ethyl-1-piperazinecarboxylate are summarized in Table 4.10 with details information such as peak area, peak level, molecular formula, molecular weight and identity. The obtained results of two samples D09DEA4MPZ2M and D10DEA7MPZ2M have no much difference it is very similar between each other only few additional peaks are found for D10DEA7MPZ2M. Two additional DGPs are 1-(2-aminoethyl)-piperazine and 1, 4-dimethylpiperazine. On the otherhand others samples D06DEA2MPZ1M, D07DEA2MPZ2M and D08DEA3MPZ2M do not show these DGPs. Based on the found results it could be reported that D10DEA7MPZ2M has lower degradation resistance than all activated DEA.

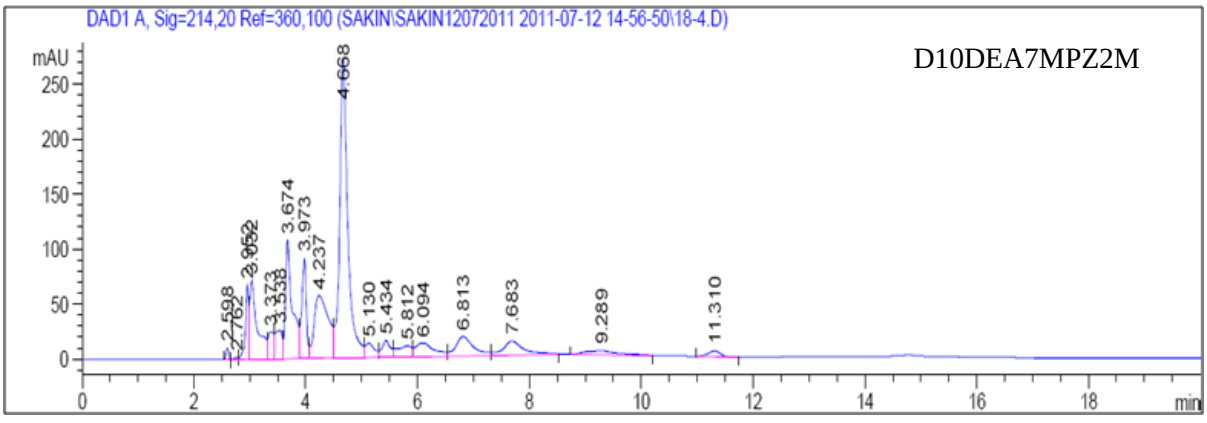


Figure 4.12: Chromatograms of carbon dioxide induced degradation of D10DEA7MPZ2M identified by HPLC-UV method.

Table 4.10: List of carbon dioxide induced degradation products of D10DEA7MPZ2M identified by HPLC-UV method

DS: DEA+H_2O+CO_2, T-100 ˚C, P-1.00 atm, L_α: 0.30, R_α: 0.73, [DEA/PZ]: 7/2, Method: HPLC (UV)									
Sample Code	**Peak No**	**Observed RT of Peck**	**Peak Level**	**Peak Area (%)**	**RT of Standard**	**Standard Verification**	**M. Formula**	**M. Weight**	**Identity**
D10DEA7MPZ2M	1	2.598	51	0.404	2.601	Detected	H_2O	18.00	Water
	2	2.762	-	0.116	-	X	-	-	UN
	3	2.952	-	3.224	-	X	-	-	UN
	4	3.032	17	8.156	2.996	Detected	$HCONH_2$	45.04	Formamide
	5	3.373	-	2.135	-	X	-	-	UN
	6	3.538	-	2.697	-	X	-	-	UN
	7	3.674	-	11.145	-	X	-	-	UN
	8	3.973	34	6.125	3.745	Detected	$C_3H_8O_2$	76.09	2-Methoxyethanol
	9	4.237	-	12.108	-	X	-	-	UN
	10	4.668	27	32.785	4.772	Detected	$C_4H_{11}NO_2$	105.14	2-(2-aminoethoxy)ethanol
	11	5.130	-	1.784	-	X	-	-	UN
	12	5.434	-	1.922	-	X	-	-	UN
	13	5.812	4	2.228	5.638	Detected	$C_6H_{15}N_3$	129.20	1-(2-Aminoethyl)piperazine
	14	6.094	-	3.458	-	X	-	-	UN
	15	6.813	18	4.755	6.754	Detected	$C_6H_{14}N_2$	114.19	1,4-Dimethylpiperazine
	16	7.683	15	4.167	7.776	Detected	$C_7H_{14}N_2O_2$	158.20	Ethyl 1-piperazinecarboxylate
	17	9.289	-	1.848	-	X	-	-	UN
	18	11.310	-	0.937	-	X	-	-	UN

N.B: UN-Unknown, RT-Retention Time (Min), X- Does Not Match

4.1.3.6 Variation of Peak Areas of Identified DGPs of DEA+H_2O+CO_2 System

Figure 4.13 represents the variation of peak areas of D06DEA2MPZ1M, D07DEA2MPZ2M and D08DEA3MPZ2M with identified degradation products. The major degradation products of D06DEA2MPZ1M are formamide (FM), 2-methoxyethanol (MOE), 2-(2-aminoethoxy) ethanol (AEE), Acetone (AC) and Ethyl-1-piperazinecarboxylate (EPC) and among these DGPs, AEE posses highest peak area, other are less than 10%. The major degradation products of D07DEA2MPZ2M are FM, MOE, AEE and EPC. MOE and FM shows highest peak area than others peaks. On the other hand for D08DEA3MPZ2M, the same degradation products are found were as FM and MOE posses highest peak areas. The variation of peak ares of each DGPs for all samples are randomly changed with amine concentration, no trends were not observed.

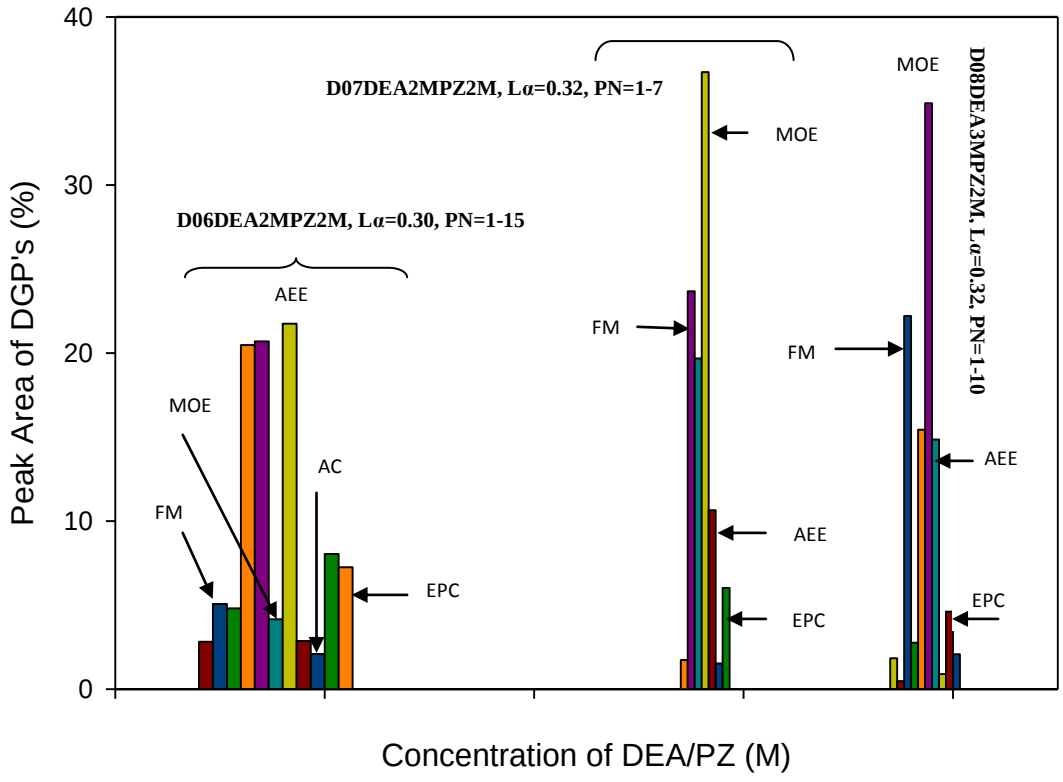


Figure 4.13: Variation of peak areas of D06DEA2MPZ1M, D07DEA2MPZ2M and D08DEA3MPZ2M identified by HPLC (UV) methods.

Figure 4.14 shows the variation of peak areas of D09DEA4MPZ2M and D10DEA7MPZ2M with identified common degradation products formamide (FM), 2-methoxyethanol (MOE), 2-(2-aminoethoxy) ethanol (AEE), 1-(2-Aminoethyl) piperazine (AEP), 1, 4-dimethylpiperazine (DMP) and ethyl-1-piperazinecarboxylate (EPC). In this figure comparatively AEE posses highest peak areas than all DGPs. FM and MOE were found to posses less than 15% peak areas which decreases with amine concentration. Peak ares AEP, DMP and EPC are increases with amine concentration.

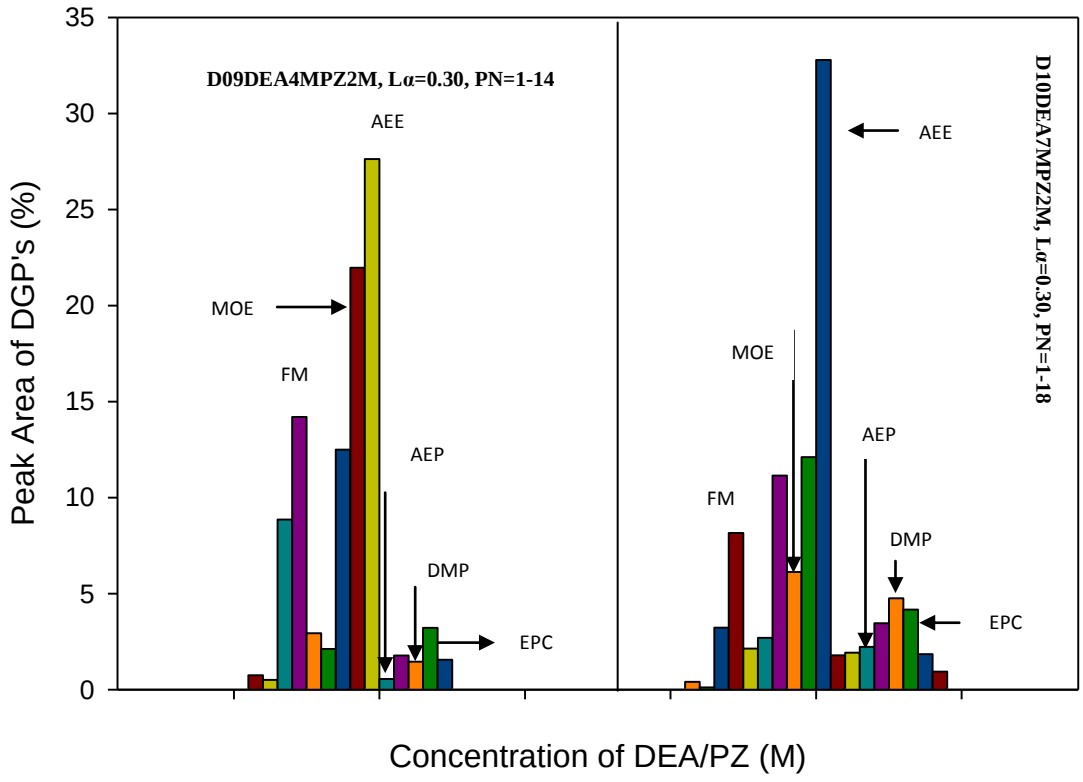


Figure 4.14: Variation of peak areas of D09DEA4MPZ2M and D10DEA7MPZ2M identified by HPLC (UV) method.

4.1.4 Degradation Products of MDEA/H_2O/CO_2 System

Various concentrations of MDEA samples such as D11MDEA2M, D12MDEA3M and D13MDEA4M were prepared and degraded by CO_2 and analyzed by HPLC-UV methods. The found results of MDEA+H_2O+CO_2 degradation system are discussed in the following section.

4.1.4.1 Degradation Products of D11MDEA2M

The chromatogram showed in figure 4.15 which reavels five peaks. Peak number one is detected for water and five is identified for MDEA which is the mother solution. Two degradation products are identified which are formamide and 2-methoxyethanol both DGPs are molecular species. Table 4.11 summarizes the degradation products of MDEA.

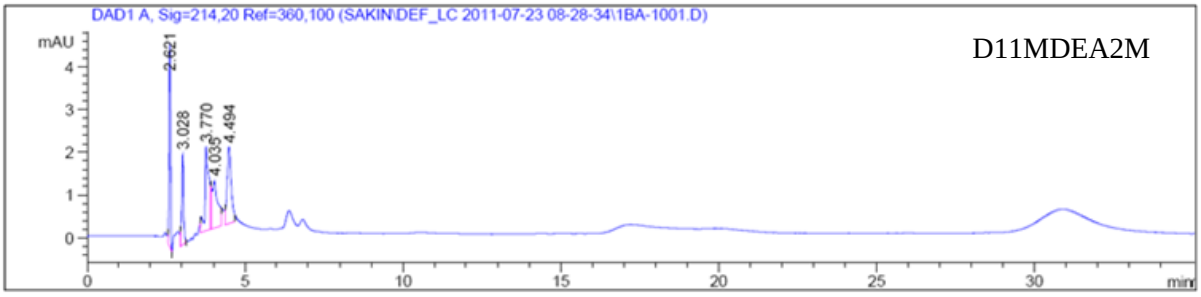


Figure 4.15: Chromatograms of carbon dioxide induced degradation of D11MDEA2M identified by HPLC-UV method.

4.1.4.2 Degradation Products of D12MDEA3M

D12MDEA3M consists of 3M methyldiethanolamine (MDEA), it's chromatogram is shown in figure 4.16. There are three peaks are observed, one is detected for water and others are identified for formamide and 2-methoxyethanolare summarized in the table 4.12.

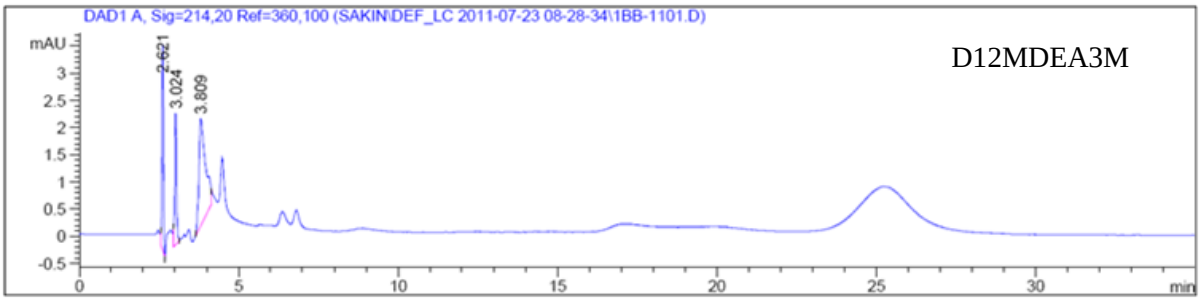


Figure 4.16: Chromatograms of carbon dioxide induced degradation of D12MDEA3M identified by HPLC-UV method.

4.1.4.3 Degradation Products of D13MDEA4M

D13MDEA4M consists of 4M methyldiethanolamine (MDEA) and its chromatogram shown in the figure 4.17. Five peaks are observed and identified. Peak number one is detected for water. Similarly the peak numbers three and five are identified for formamide and 2-methoxyethanol respectively are given in Table 4.13.

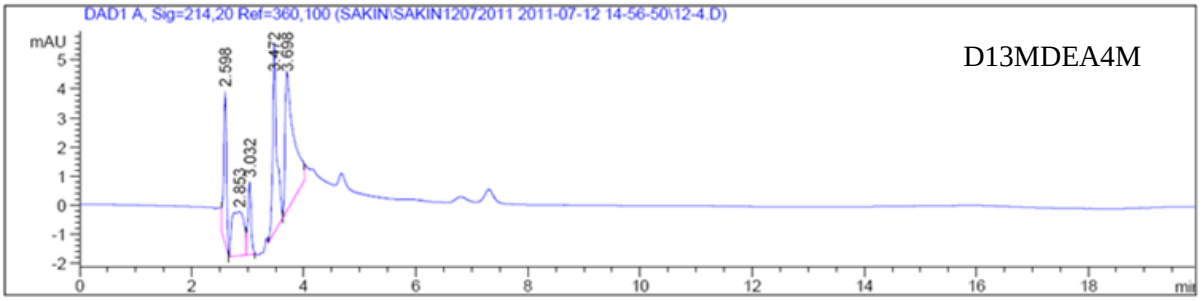


Figure 4.17: Chromatograms of carbon dioxide induced degradation of D13MDEA4M identified by HPLC-UV method.

While MDEA was initially thought of as non degradable, recently it has been argued by many researchers that MDEA often degrades in tail gas treating unit (TGTU) services, and efforts are being reflected on improved reclaiming options for solvent quality control. MDEA molecule degrades into HSS, DEA, MMEA and bicine. Bis-(hydroxyethyl)glycine also known as 'Bicine' is a degradation product formed in the presence of DEA and unstable chemical intermediates (Closmann et al., 2009; Closmann, 2009; Sargent and Howard, 2003). Monomethylethanolamine (MMEA) is one of the simpler amines that may be formed from MDEA degradation, since MMEA is a secondary amine; it will react directly with CO_2. Diethanolamine (DEA) is a secondary amine that may be formed from MDEA. Since DEA is a secondary amine, it will react directly with CO_2 as well.

Table 4.11: List of carbon dioxide induced degradation products of D11MDEA2M identified by HPLC-UV method

DS: MDEA+H_2O+CO_2, T-100 ˚C, P-1.00 atm, L_α: 0.10, R_α: 0.18, [MDEA]: 2M, Method: HPLC (UV)									
Sample Code	**Peak No**	**Observed RT of Peck**	**Peak Level**	**Peak Area (%)**	**RT of Standard**	**Standard Verification**	**M. Formula**	**M. Weight**	**Identity**
D11MDEA2M	1	2.621	51	21.365	2.601	Detected	H_2O	18.00	Water
	2	3.028	17	12.307	2.996	Detected	$HCONH_2$	45.04	Formamide
	3	3.770	34	23.644	3.745	Detected	$C_3H_8O_2$	76.09	2-Methoxyethanol
	4	4.035	-	20.631	-	X	-	-	UN
	5	4.494	23	22.051	4.911	Detected	C5H13NO2	119.16	Methyldiethanolamine

N.B: UN-Unknown, RT-Retention Time (Min), X- Does Not Match

Table 4.12: List of carbon dioxide induced degradation products of D12MDEA3M identified by HPLC-UV method

DS: MDEA+H_2O+CO_2, T-100 ˚C, P-1.00 atm, L_α: 0.1, R_α: 0.2, [MDEA]: 3M, Method: HPLC (UV)									
Sample Code	**Peak No**	**Observed RT of Peck**	**Peak Level**	**Peak Area (%)**	**RT of Standard**	**Standard Verification**	**M. Formula**	**M. Weight**	**Identity**
D12MDEA3M	1	2.621	51	25.008	2.601	Detected	H_2O	18.00	Water
	2	3.024	17	19.312	2.996	Detected	$HCONH_2$	45.04	Formamide
	3	3.809	34	55.679	3.745	Detected	$C_3H_8O_2$	76.09	2-Methoxyethanol

N.B: UN-Unknown, RT-Retention Time (Min), X- Does Not Match

Table 4.13: List of carbon dioxide induced degradation products of D13MDEA4M identified by HPLC-UV method

DS: MDEA+H_2O+CO_2, T-100 ˚C, P-1.00 atm, L_α: 0.10, R_α: 0.20, [MDEA]: 4M, Method: HPLC (UV)									
Sample Code	**Peak No**	**Observed RT of Peck**	**Peak Level**	**Peak Area (%)**	**RT of Standard**	**Standard Verification**	**M. Formula**	**M. Weight**	**Identity**
D13MDEA4M	1	2.598	51	13.968	2.601	Detected	H_2O	18.00	Water
	2	2.853	-	17.128	-	X	-	-	UN
	3	3.032	17	7.414	2.996	Detected	$HCONH_2$	45.04	Formamide
	4	3.472	-	24.890	-	X	-	-	UN
	5	3.698	34	36.598	3.745	Detected	$C_3H_8O_2$	76.09	2-Methoxyethanol

N.B: UN-Unknown, RT-Retention Time (Min), X- Does Not Match

4.1.4.4 Variation of Peak Areas of MDEA+H_2O+CO_2 System

Figure 4.18 represents the degradation products of D11MDEA2M, D12MDEA3M and D13MDEA4M with peak areas. The major DGPs of the avove mentioned three samples are Formamide (FM) and 2-Methoxyethanol (MOE). The peak area of FM and MOE for D11MDEA2M and D12MDEA3M increases with amine concentrations but decreases for D13MDEA4M. MOE posses highest peak areas for three samples. The overall peak ares foe all DGPs were not found to follow any trends, it is randomly changes with amine concentration.

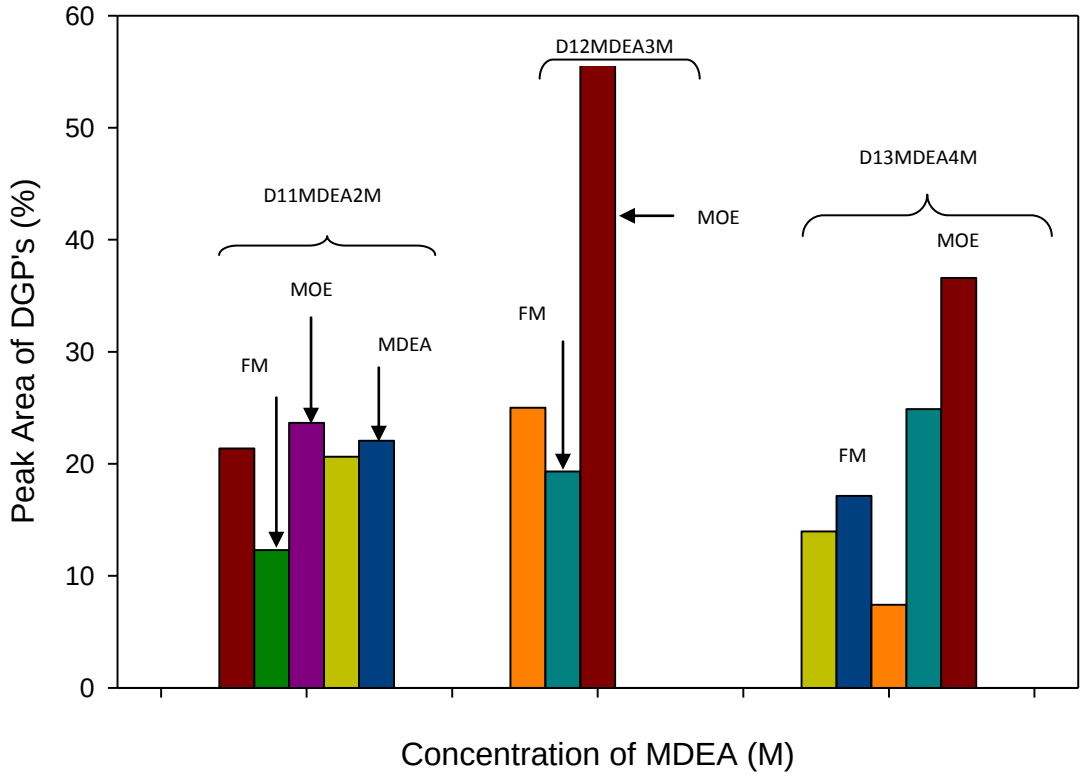


Figure 4.18: Variation of peak areas of D11MDEA2M, D12MDEA3M and D13MDEA4M identified by HPLC (UV) methods.

4.1.5 Degradation Products of MDEA+PZ+H_2O+CO_2 System

Ffive activated samples D14MDEA2MPZ1M, D15MDEA2MPZ2M, D16MDEA3MPZ2M, D17MDEA4MPZ2M and D18MDEA7MPZ2M were prepared and degraded under predetermined experimental condition.

4.1.5.1 Degradation Products of D14MDEA2MPZ1M

This sample consists of 2M methyldiethanolamine and 1M piperazine. The observed chromatogram of this sample shown in figure 4.19 which reavels four peaks and all are identified. Peak number one is detected for DDW. Peaks number two, three and four were found as formamide, 2-methoxymethanol and ethanol respectively. MDEA is a stable amine has greater resistance to degradation as compared to secondary and primary amines. By comparing with inactivated samples such as D11MDEA2M, D12MDEA3M and D13MDEA4M activated sample showed low DGP. In addition activated MDEA and inactivated MDEA up to 4M concentration no significant change was found. The identified degradation products of sample (D14MDEA2MPZ1M) are formamide, ethanol and 2-methoxyethanol. The oxidation of amine produces alcohol, aldehyde and acid was reported by many authors (Supap et al., 2006; M. S.Islam, 2010; Lepaumier et al., 2009c). Further the amine and acid react to form amides which are also reported in the open literature (Freeman et al., 2009). 2-methoxyethanol is a derivative of ethanol was found as new degradation products.

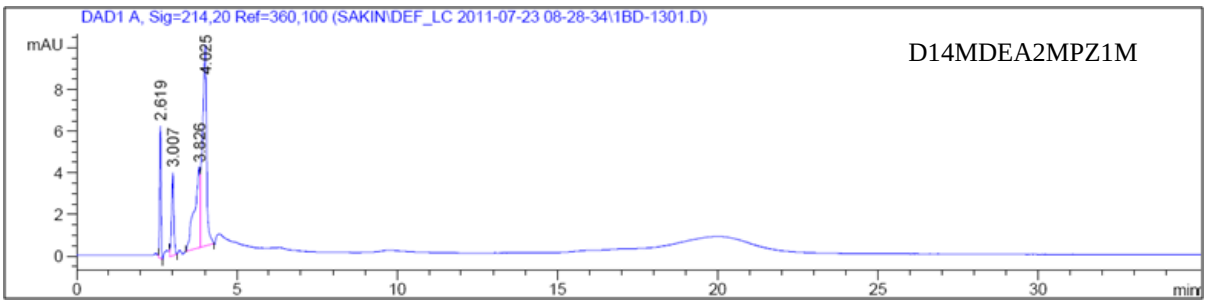


Figure 4.19: Chromatograms of carbon dioxide induced degradation of D14MDEA2MPZ1M identified by HPLC-UV method.

4.1.5.2 Degradation Products of D15MDEA2MPZ2M

The observed chromatogram of this sample is shown in Figure 4.20. Four peaks were observed in the chromatogram and all are identified. Peak number one is detected for DDW. Peaks number two, three and four were found as formamide, 2-methoxymethanol and ethanol respectively. MDEA is very stable amine have greater resistance to degradation over secondary and primary amines. By comparing with inactivated samples such as D11MDEA2M, D12MDEA3M and D13MDEA4M activated sample showed low DGP. In addition activated MDEA and inactivated MDEA up to 4M concentration no significant change was followed in this study. Activated two samples D14MDEA2MPZ1M and D15MDEA2MPZ2M showed same degradation products. Table 4.15 showed details information of the identified DGPs of D15MDEA2MPZ2M sample. The results are in accordance with that reported by many researchers (Supap et al., 2006; Lepaumier et al., 2009c, b; Haws, 2010).

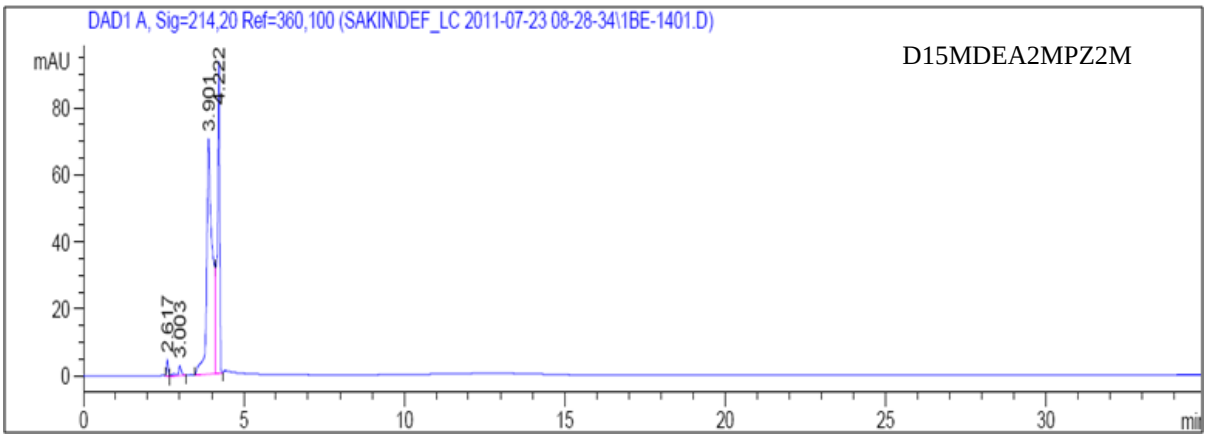


Figure 4.20: Chromatograms of carbon dioxide induced degradation of D15MDEA2MPZ2M identified by HPLC-UV method.

Table 4.14: List of carbon dioxide induced degradation products of D14MDEA2MPZ1M identified by HPLC-UV method

DS: MDEA+PZ+H_2O+CO_2, T-100 ˚C, P-1.00 atm, L_α: 0.20, R_α: 0.45, [MDEA/PZ]: 2/1, Method: HPLC (UV)									
Sample Code	**Peak No**	**Observed RT of Peck**	**Peak Level**	**Peak Area (%)**	**RT of Standard**	**Standard Verification**	**M. Formula**	**M. Weight**	**Identity**
D14MDEA2MPZ1M	1	2.619	51	11.447	2.601	Detected	H_2O	18.00	Water
	2	3.007	17	11.010	2.996	Detected	$HCONH_2$	45.04	Formamide
	3	3.826	34	25.618	3.745	Detected	$C_3H_8O_2$	76.09	2-Methoxyethanol
	4	4.025	46	51.923	4.117	Detected	C_2H_6O	46.07	Ethanol

N.B: UN-Unknown, RT-Retention Time (Min), X- Do Not Match

Table 4.15: List of carbon dioxide induced degradation products of D15MDEA2MPZ2M identified by HPLC-UV method

DS: MDEA+PZ+H_2O+CO_2, T-100 ˚C, P-1.00 atm, L_α: 0.20, R_α: 0.48, [MDEA/PZ]: 2/2, Method: HPLC (UV)									
Sample Code	**Peak No**	**Observed RT of Peck**	**Peak Level**	**Peak Area (%)**	**RT of Standard**	**Standard Verification**	**M. Formula**	**M. Weight**	**Identity**
D15MDEA2MPZ2M	1	2.617	51	1.084	2.601	Detected	H_2O	18.00	UPW
	2	3.003	17	1.622	2.996	Detected	$HCONH_2$	45.04	Formamide
	3	3.901	34	62.519	3.745	Detected	$C_3H_8O_2$	76.09	2-Methoxyethanol
	4	4.222	46	34.773	4.117	Detected	C_2H_6O	46.07	Ethanol

N.B: UN-Unknown, RT-Retention Time (Min), X- Do Not Match

4.1.5.3 Degradation Products of D16MDEA3MPZ2M

D16MDEA3MPZ2M activated sample contains 3M methyldiethanolamine and 2M piperazine its chromatogram is given in figure 4.21 and the chromatogram is similar to that of previous sample D15MDEA2MPZ2M. However, four peaks were found in this chromatogram and all are identified. Peak number one is for DDW, on the other hand peaks number two, three and four are found as formamide, 2-methoxymethanol and ethanol respectively. The probable reasons of greater degradation resistance of MDEA over secondary and primary amines are that MDEA has higher molecular weight than MEA or DEA, and high boiling point and low vapor pressure (Closmann et al., 2009). Comparing MDEA (D11MDEA2M, D12MDEA3M and D13MDEA4M) to activated sample shows lower peaks of DGPs. Activated samples are D14MDEA2MPZ1M, D15MDEA2MPZ2M and D16MDEA3MPZ2M showed the same degradation products, regardless of amine concentration. Table 4.16 shows the details information of identified DGPs of D16MDEA3MPZ2M sample.

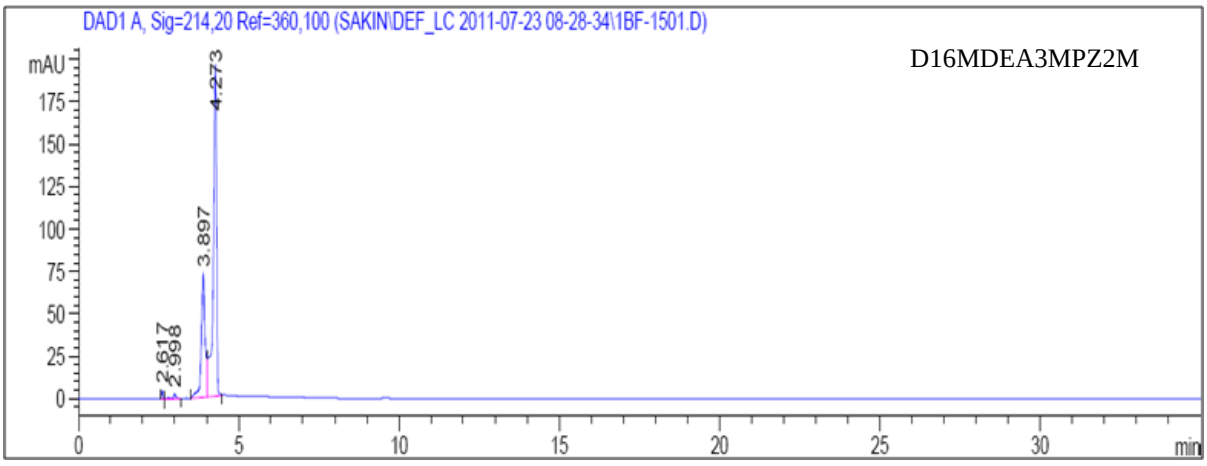


Figure 4.21: Chromatograms of carbon dioxide induced degradation of D16MDEA3MPZ2M identified by HPLC-UV method.

4.1.5.4 Degradation Products of D17MDEA4MPZ2M

Degraded D17MDEA4MPZ2M sample consists of 4M methyldiethanolamine and 2M piperazine, its chromatogram is given in figure 4.22. These results are similar to that of activated samples of MDEA such as D14MDEA2MPZ1M, D15MDEA2MPZ2M and D16MDEA3MPZ2M. It is reported that these DGPs are distinguishable by considering occurred concentration, retention time and peak area. However, four peaks are found, peak number two, three and four were identified as formamide, 2-methoxymethanol and ethanol respectively are shows in the figure 4.22.

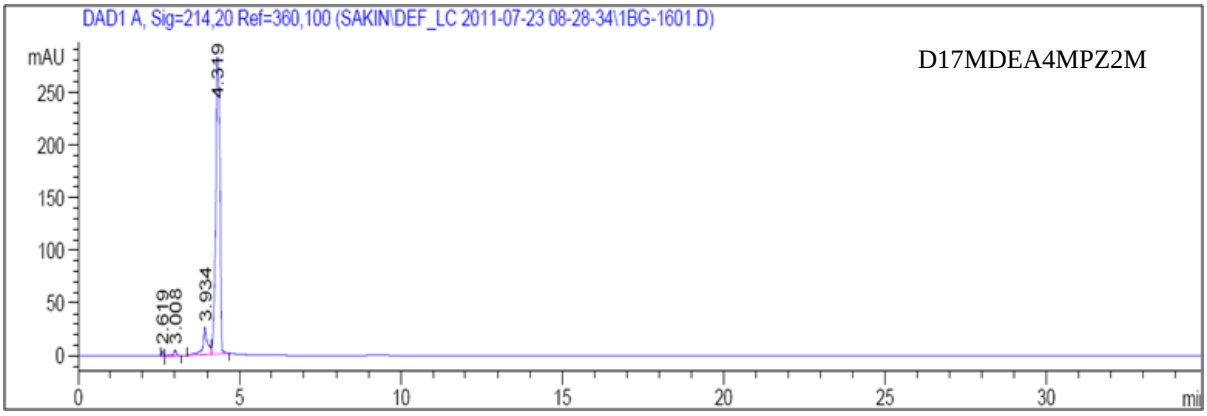


Figure 4.22: Chromatograms of carbon dioxide induced degradation of D17MDEA4MPZ2M identified by HPLC-UV method.

Table 4.16: List of carbon dioxide induced degradation products of D16MDEA3MPZ2M identified by HPLC-UV method

System: MDEA+H_2O+CO_2, T-100 ˚C, P-1.00 atm, L_α: 0.20, R_α: 0.50, [MDEA/PZ]: 3/2, Method: HPLC (UV)									
Sample Code	**Peak No**	**Observed RT of Peck**	**Peak Level**	**Peak Area (%)**	**RT of Standard**	**Standard Verification**	**M. Formula**	**M. Weight**	**Identity**
D16MDEA3MPZ2M	1	2.617	51	0.729	2.601	Detected	H_2O	18.00	Water
	2	2.998	17	0.974	2.996	Detected	$HCONH_2$	45.04	Formamide
	3	3.897	34	29.083	3.745	Detected	$C_3H_8O_2$	76.09	2-Methoxyethanol
	4	4.273	46	69.212	4.117	Detected	C_2H_6O	46.07	Ethanol

N.B: UN-Unknown, RT-Retention Time (Min), X- Do Not Match

Table 4.17: List of carbon dioxide induced degradation products of D17MDEA4MPZ2M identified by HPLC-UV method

DS: MDEA+PZ+H_2O+CO_2, T-100 ˚C, P-1.00 atm, L_α: 0.20, R_α: 0.50, [MDEA/PZ]: 4/2, Method: HPLC (UV)									
Sample Code	**Peak No**	**Observed RT of Peck**	**Peak Level**	**Peak Area (%)**	**RT of Standard**	**Standard Verification**	**M. Formula**	**M. Weight**	**Identity**
D17MDEA4MPZ2M	1	2.619	51	0.511	2.601	Detected	H_2O	18.00	Water
	2	3.008	17	1.288	2.996	Detected	$HCONH_2$	45.04	Formamide
	3	3.934	34	9.029	3.745	Detected	$C_3H_8O_2$	76.09	2-Methoxyethanol
	4	4.319	46	89.170	4.117	Detected	C_2H_6O	46.07	Ethanol

N.B: UN-Unknown, RT-Retention Time (Min), X- Do Not Match

4.1.5.5 Degradation Products of D18MDEA7MPZ2M

D18MDEA7MPZ2M consists of 7M methyldiethanolamine and 2M piperazine its chromatogram is shown in the Figure 4.23. Identified DGPs are similar to that of activated samples D14MDEA2MPZ1M, D15MDEA2MPZ2M, D16MDEA3MPZ2M and D17MDEA4MPZ2M but on the basis of total numbers of peaks, occured DGPs concentration and peak's areas these parameters are distinguishable between each other. However, six peaks are identified and peak number one is detected for water it is not treated as degradation products. Peak number three, five and six are found for formamide, 2-methoxymethanol and ethanol respectively which shown in Table 4.18.

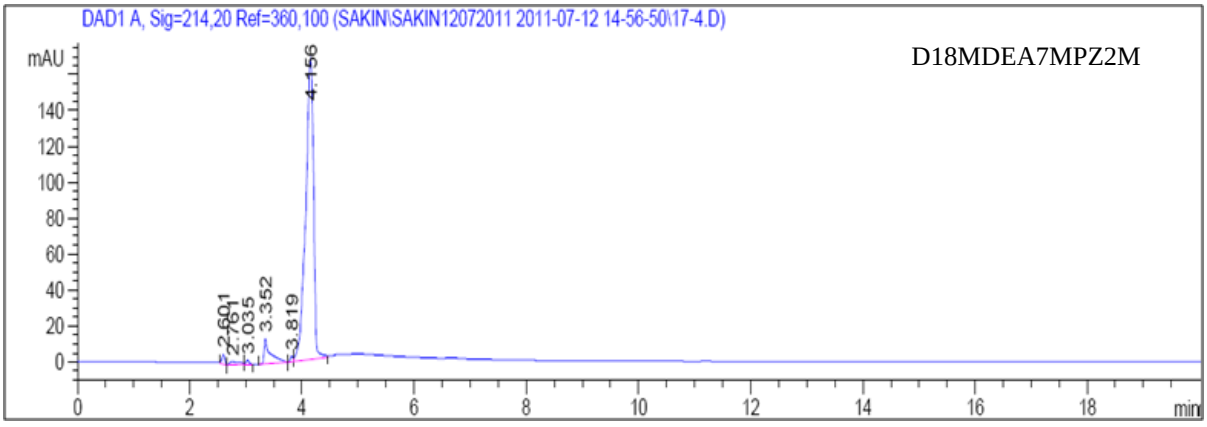


Figure 4.23: Chromatograms of carbon dioxide induced degradation of D18MDEA7MPZ2M identified by HPLC-UV method.

Table 4.18: List of carbon dioxide induced degradation products of D18MDEA7MPZ2M identified by HPLC-UV method

DS: MDEA+PZ+H_2O+CO_2, T-100 ˚C, P-1.00 atm, L_α: 0.23, R_α: 0.50, [MDEA/PZ]: 7/2, Method: HPLC (UV)									
Sample Code	**Peak No**	**Observed RT of Peck**	**Peak Level**	**Peak Area (%)**	**RT of Standard**	**Standard Verification**	**M. Formula**	**M. Weight**	**Identity**
D18MDEA7MPZ2M	1	2.601	51	1.031	2.601	Detected	H_2O	18.00	Water
	2	2.761	-	1.261	-	X	-	-	UN
	3	3.035	17	0.591	2.996	Detected	$HCONH_2$	45.04	Formamide
	4	3.352	-	6.039	-	X	-	-	UN
	5	3.819	34	0.596	3.745	Detected	$C_3H_8O_2$	76.09	2-Methoxyethanol
	6	4.156	46	90.479	4.117	Detected	C_2H_6O	46.07	Ethanol

N.B: UN-Unknown, RT-Retention Time (Min), X- Do Not Match, DS- Degradation System

4.1.5.6 Variation of Peak Areas of MDEA+PZ+H_2O+CO_2 System

Figure 4.24 shows the peak areas for five activated MDEA samples D14MDEA2MPZ1M, D15MDEA2MPZ2M, D16MDEA3MPZ2M, D17MDEA4MPZ2M ad D18MDEA7MPZ2M. The common degradation products for all activated samples are 2-methoxymethanol (MOE) and ethanol (EN). Formamide is identified for D18MDEA7MPZ2M and D14MDEA2MPZ1M. EN and MOE in this bar diagram shows highest peak areas. Therefore, the identified DGPs were found not to follow any trends of peak areas with amine concentration.

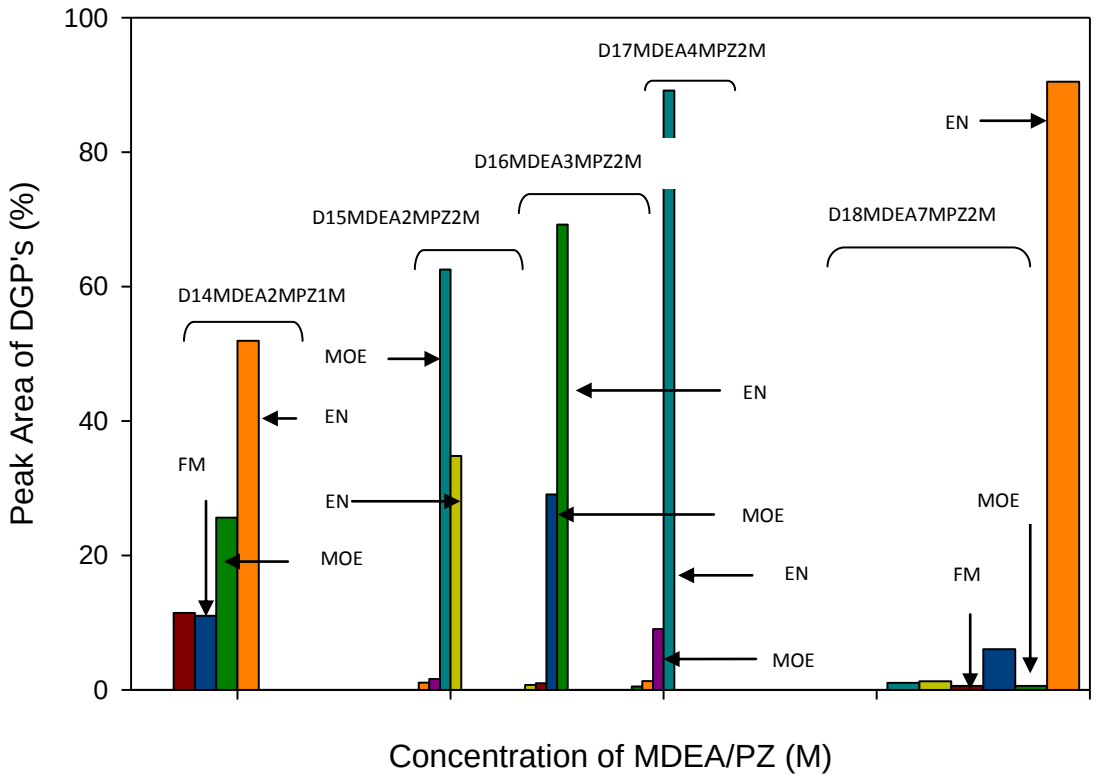


Figure 4.24: Variation of peak areas of identified DGPs of D14MDEA2MPZ1M, D15MDEA2MPZ2M, D16MDEA3MPZ2M, D17MDEA4MPZ2M and D18MDEA7MPZ2M identified by HPLC (UV) method

4.1.6 Summary of HPLC (UV) Analysis

In this section, the identified degradation products are explained for five dedradation systems. During the analysis some additional compounds are also detected these are for as example water and base amine components. The base amines are DEA, MDEA and PZ which are not degradation products though it was shown in the following table. The identified degradation products of PZ+H_2O+CO_2 System for D01PZ1M and D02PZ2M samples are summarized in table 4.19. The main identified degradation products of this system are formamide, 2-methoxy ethanol and 2-(2-aminoethoxy)-ethanol. Freeman and Sexton separately studied the degradation behavior of PZ and both are reported formamide as a degradation product (Freeman et al., 2009; Sexton, 2008). Based on the found results the degradation stability of these two samples was found to follow this order D01PZ2M> D01PZ1M.

Table: 4.19: Degradation Products of PZ+H_2O+CO_2 System Identified by HPLC-UV Method

Sample Code	M. Formula	M. Weight	Identity
DO1PZ1M	H_2O	18.00	Water
	$HCONH_2$	45.04	Formamide
	$C_4H_{11}NO_2$	105.14	2-(2-aminoethoxy)ethanol
	$C_3H_8O_2$	76.09	2-Methoxyethanol
DO2PZ2M	H_2O	18.00	Water
	$HCONH_2$	45.04	Formamide
	$C_3H_8O_2$	76.09	2-Methoxyethanol

The identified degradation products of DEA+H_2O+CO_2 System for DO3DEA2M, DO4DEA3M and DO5DEA4M are summarized in table 4.20. The identified degradation products of DO3DEA2M are formamide, 2-methoxyethanol, diethylenetriamine, 2-(2-aminoethoxy)-ethanol, triethanolamine, acetone and Ethyl 1-piperazinecarboxylate. Nevertheless, the degradation products of DO4DEA3M are found seven which are same as D03DEA2M and D05DEA4M, but D05DEA4M only showed one additional degradation product which is ethanol.

Diethanolamine is generally degraded and breakdown into monoethanolamine and both amines are capable to produce acids and alcohol (Dawodu and Meisen, 1991; M. S.Islam, 2010). There is an another experiment on the degradation of MEA induced by carbon dioxide and reported acetone, ethanol, acetate and amides as DGP identified by HPLC and GC-MS (Supap et al., 2006). Based on the number of peaks high concentrated sample degraded more. In this work finally the order of degradation resistance was found D03DEA2M> D04DEA3M> D05DEA4M.

Table 4.20: Degradation Products of DEA+H_2O+CO_2 System Identified by HPLC-UV Method

Sample Code	M. Formula	M. Weight	Identity
DO3DEA2M & D04DEA3M	H_2O	18.00	Water
	$HCONH_2$	45.04	Formamide
	$C_3H_8O_2$	76.09	2-Methoxyethanol
	$C_4H_{13}N_3$	103.17	Diethylenetriamine
	$C_4H_{11}NO_2$	105.14	2-(2-aminoethoxy)ethanol
	$C_6H_{15}NO_3$	149.19	Triethanolamine (TEA)
	C_3H_6O	58.08	Acetone
	$C_7H_{14}N_2O_2$	158.20	Ethyl 1-piperazinecarboxylate
DO5DEA4M	The degradation products of D05DEA4M were found same as D03DEA2M and D03DEA2M with one additional degradation product which is Ethanol (M.Wet 46.07)		

The identified degradation products DEA+PZ+H_2O+CO_2 System for five degraded samples D06DEA2MPZ1M, D07DEA2MPZ2M, D08DEA3MPZ2M, D09DEA4MPZ2M and D10DEA7MPZ2M are summarized in table 4.21. First sample D06DEA2MPZ1M showed five degradation products these are formamide, 2-methoxyethanol, 2-(2-aminoethoxy)-ethanol, acetone and Ethyl-1-piperazinecarboxylate. The second and third samples D07DEA2MPZ2M and D08DEA3MPZ2M are shows four degradation products these are formamide, 2-methoxyethanol, 2-(2-aminoethoxy)-ethanol and Ethyl-1-piperazinecarboxylate. The identified DGPs of D09DEA4MPZ2M and D10DEA7MPZ2M are formamide, 2-methoxyethanol, 2-(2-aminoethoxy)-ethanol, 1-(2-Aminoethyl)-piperazine, 1, 4-dimethylpiperazine and Ethyl-1-piperazinecarboxylate. Depending on the

found result it is concluded that degradation stability of these five samples follow this order i.e. D06DEA2MPZ2M>D07DEA2MPZ1M>D08DEA3MPZ2M>D09DEA4MPZ2M> D10DEA7MPZ2M.

Table 4.21: Degradation Products of DEA+PZ+H_2O+CO_2 System Identified by HPLC-UV Method

Sample Code	M. Formula	M. Weight	Identity
D06DEA2MPZ1M	This sample shows one additional degradation products which is acetone otherwise the others DGPs are same as D07DEA2MPZ2M and D08DEA3MPZ2M		
D07DEA2MPZ2M & D08DEA3MPZ2M	H_2O	18.00	Water
	$HCONH_2$	45.04	Formamide
	$C_3H_8O_2$	76.09	2-Methoxyethanol
	$C_4H_{11}NO_2$	105.14	2-(2-aminoethoxy)ethanol
	$C_7H_{14}N_2O_2$	158.20	Ethyl 1-piperazinecarboxylate
D09DEA4MPZ2M & D10DEA7MPZ2M	H_2O	18.00	Water
	$HCONH_2$	45.04	Formamide
	$C_3H_8O_2$	76.09	2-Methoxyethanol
	$C_4H_{11}NO_2$	105.14	2-(2-aminoethoxy)ethanol
	$C_6H_{15}N_3$	129.20	1-(2-Aminoethyl) piperazine
	$C_6H_{14}N_2$	114.19	1,4-Dimethylpiperazine
	$C_7H_{14}N_2O_2$	158.20	Ethyl 1-piperazinecarboxylate

Several compounds that have been identified as degradation products for three different inactivated degraded samples of MDEA+H_2O+CO_2 System are summarized in table 4.22. The degraded samples are D11MDEA2M, D12MDEA3M and D13MDEA4M. The degradation products of these three samples are namely formamide and 2-methoxyethanol. Acid and amine is the best couple to react between each other for the formation of amides or further products. Amide was found as a degradation product significantly in the open literature too (Freeman, 2010; Freeman et al., 2009). 2-methoxyethanol is a derivative of ethanol was found as new degradation products. Based on the literature survey it could be treated as new DGP.

By comparing this result with inactivated DEA samples obviously MDEA is more stable than DEA nevertheless activated diethanolamine is not found better resistance than MDEA.

Table: 4.22: Degradation Products of MDEA+H_2O+CO_2 System Identified by HPLC-UV Method

Sample Codes	M. Formula	M. Weight	Identity
D11MDEA2M, D12MDEA3M, D13MDEA4M	H_2O	18.00	Water
	$HCONH_2$	45.04	Formamide
	$C_3H_8O_2$	76.09	2-Methoxyethanol
	C5H13NO2	119.16	Methyldiethanolamine

Degradation products of MDEA+PZ+H_2O+CO_2 system for five degraded samples D14MDEA2MPZ1M, D15MDEA2MPZ2M, D16MDEA3MPZ2M, D17MDEA4MPZ2M and D18MDEA7MPZ2M.MDEA/PZ are summarized in table 4.23. The most common DGPs are formamide, 2-methoxyethanol and ethanol are detected. The found results are identical with open literature reported by many researchers (Supap et al., 2006; Lepaumier et al., 2009c, b; Haws, 2010). In this experiment identified DGPs of activated MDEA are found significantly lower than activated/inactivated DEA and inactivated MDEA. So, in the aqueous absorption and stripping process MDEA/PZ blends are best choice over single MDEA or DEA. Closmann reported that MDEA/PZ solvent blend provides greater stability over MEA when tested at conditions pertinent to CO_2 scrubbing in flue gas (Closmann et al., 2009).

Table: 4.23: Degradation Products of MDEA+PZ+H_2O+CO_2 System Identified by HPLC-UV Method

Sample Codes	M. Formula	M. Weight	Identity
D14MDEA2MPZ1M, D15MDEA2MPZ2M, D16MDEA3MPZ2M, D17MDEA4MPZ2M, D18MDEA7MPZ2M	H_2O	18.00	Water
	$HCONH_2$	45.04	Formamide
	$C_3H_8O_2$	76.09	2-Methoxyethanol
	C_2H_6O	46.07	Ethanol

4.2 Ion Chromatographic (IC) Methods

Three different Ion Chromatographic (IC) methods are used in this detection these are Anionic Ion Chromatographic Method (AICM), Cationic Ion Chromatographic Method (CICM) and Organic Acid Ion Chromatographic Method (OICM).

4.2.1 Degradation Products of PZ+H_2O+CO_2 System

4.2.1.1 Degradation Products of D01PZ1M

The chromatogram of anionic ion chromatographic method for D01PZ1M sample which consists of 1M piperazine is shown in figure 4.25. Two peaks are identified as acetate and phosphate in this detection. Peaks number 1, 3, 4, 5 and 7 are unidentified due to the low concentration of DGPs. The possible reason of occurred DGP acetate is that PZ molecule undergoes ring opening reaction (Lepaumier et al., 2009b) and the degraded chain of piperazine takes part to further degradation to produce acetate. In cationic ion chromatographic method (CICM) did not identify any DGP. The chromatogram is shown in figure 4.26. In the most cases cationic degradation products of carbonated PZ was found ammonia and ammonium ion as reported by many researchers (Supap et al., 2006; Kadnar R., 1999). This ammonia may exist in gaseous form, in the solution as ammonium cation or tied up with carboxylic acid as formamide or oxamide. Using cation chromatography analytical method, ammonium is eluted around the same time as MEA, which is present in concentration at least 100X greater than ammonia. As a result the ammonium peak is hidden under the MEA peak and cannot be effectively separated (Sexton, 2008). In the organic acid ion chromatographic methods the chromatogram in figure 4.21 shows two peaks but none of these are identified. Several standards of organic acids were prepared and properly calibrated in this detection. In the chromatogram peak number two is considered due to the presence of butyrate ion. The overall IC results for the sample D01PZ1M are summarized in Table 4.24. The identified anionic degradation products are acetate and phosphate.

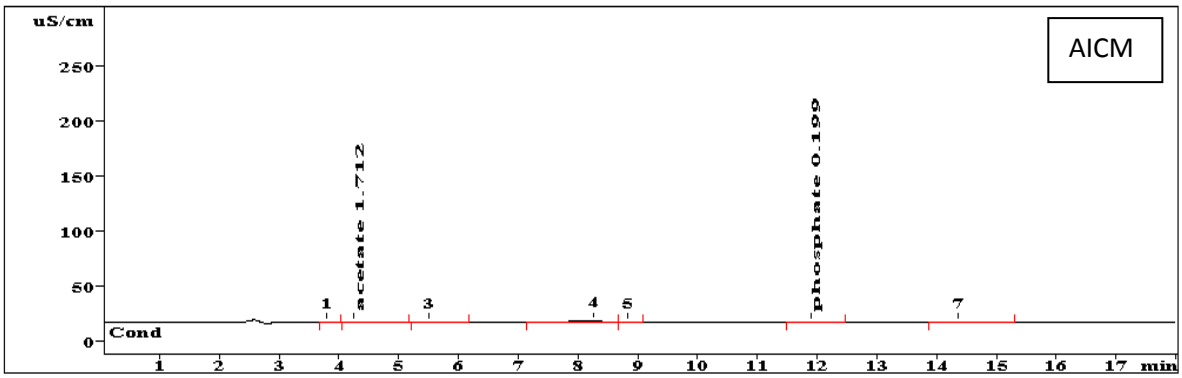


Figure 4.25: Chromatograms of CO_2 induced degradation products of D01PZ1M sample identified by AICM.

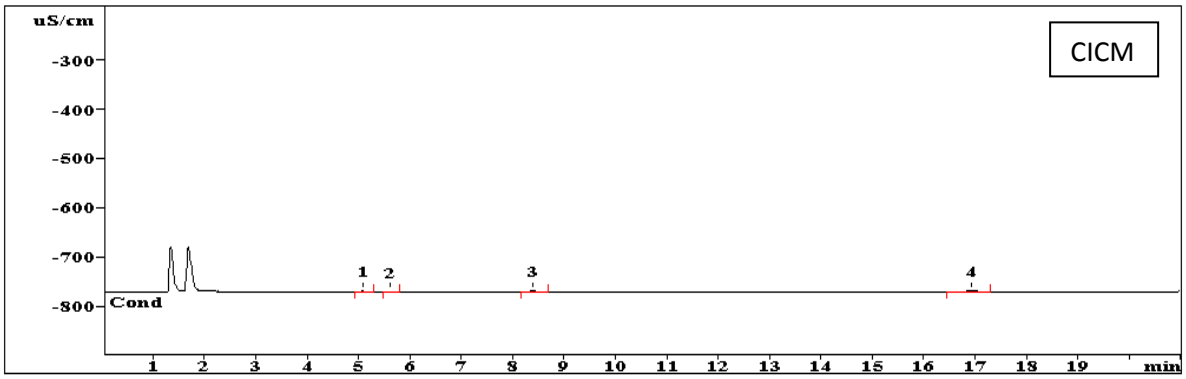


Figure 4.26: Chromatograms of CO_2 induced degradation products of D01PZ1M sample identified by CICM.

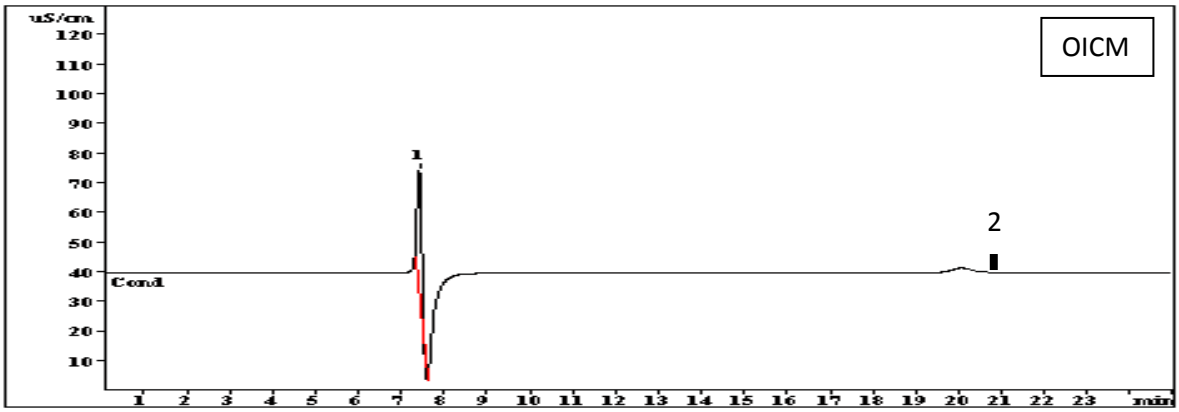


Figure 4.27: Chromatograms of CO_2 induced degradation products of D01PZ1M sample identified by OICM.

Table 4.24: Carbon dioxide induced degradation products of D01PZ1M identified by IC methods [Sample Code: D01PZ1M, Loading (α_L= 0.4, α_R = 0.6), pH (I) = 11.56, pH (F) = 8.05]

Experiment and Analysis		DGPs and Details Parameters	
Analytical Method: IC	AICM	Peck Level (PL)	1, 2, 3, 4, 5, 6, 7
		DGP (PL: 2, 6)	Act., PO_4^{3-}
		[DGP], ppm	1.712, 0.199
		Std. Verification	RT: 4.25, 11.89
	CICM	Peck Level	1, 2, 3, 4
		DGP (PL: N/A)	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A
	OICM	Peck Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A

4.2.1.2 Degradation Products of D02PZ2M

Degraded sample D02PZ2M consists of 2M piperazine is analyzed by IC methods. Figure 4.28 showed the chromatogram of AICM-01. Seven peaks are observed and peak number five is identified for nitrate. Amines are highly oxidized by air and form various oxide of nitrogen. These oxides are capable of forming nitrogenous acids in the amine system. All acids are capable to initiate the formation of heat stable salt in the amine system. Figure 4.29 shows the chromatogram of AICM-02 for the same amine sample D02PZ2M where as two peaks are observed and nitrite is identified as additional DGPs for D02PZ2M. Cationic ion chromatographic method (CICM) shows ammonium peak as reaction product in figure 4.30. Ammonium is the most common cationic DGP in amine system. The dissociation of alkanolamines in water produces many ionic products, protonated piperazine (PZH^+). OICM the chromatogram in figure 4.31 shows two peaks and none of these are detected. This is possibly due to the limitation of IC standards. But it is believed that these unknown peaks are butyrate or any other organic acids except calibrated standards.

Table 4.25 summarizes identified DGPs. Sexton and Rochelle in 2010 studied the degradation of PZ induced by carbon dioxide and analyzed the degraded PZ solution their result are in accordance with the results of this work.

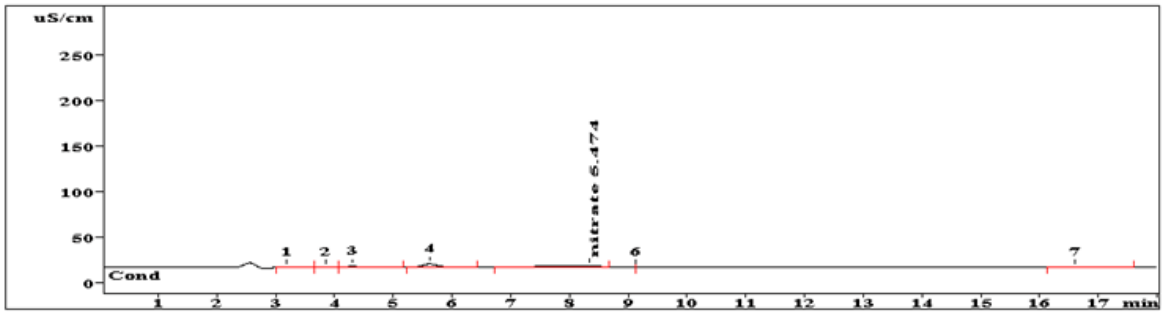


Figure 4.28: Chromatograms of CO_2 induced degradation products of D02PZ2M identified by AICM-01.

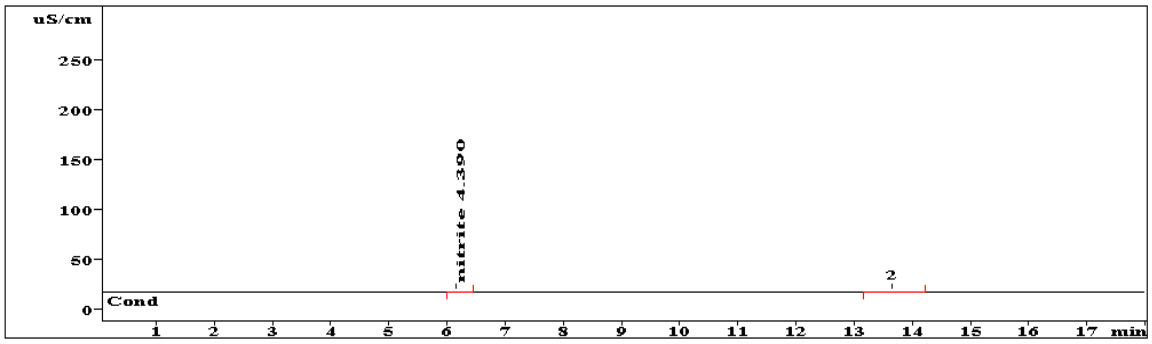


Figure 4.29: Chromatograms of CO_2 induced degradation products of D02PZ2M identified by AICM-02.

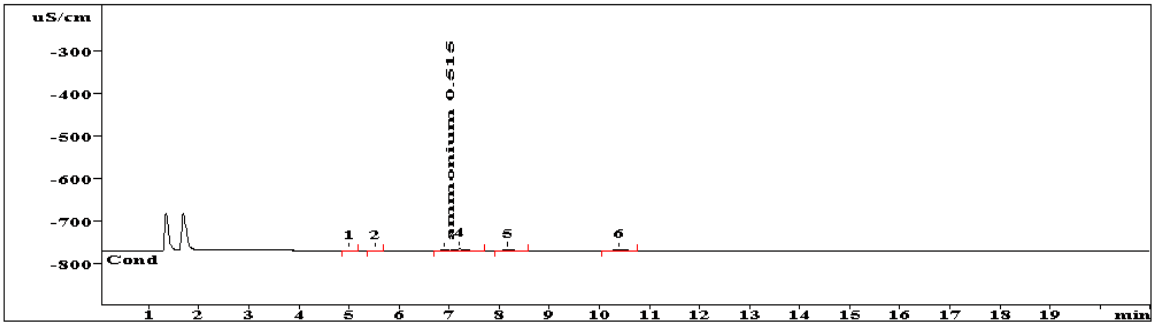


Figure 4.30: Chromatograms of CO_2 induced degradation products of D02PZ2M sample identified by CICM.

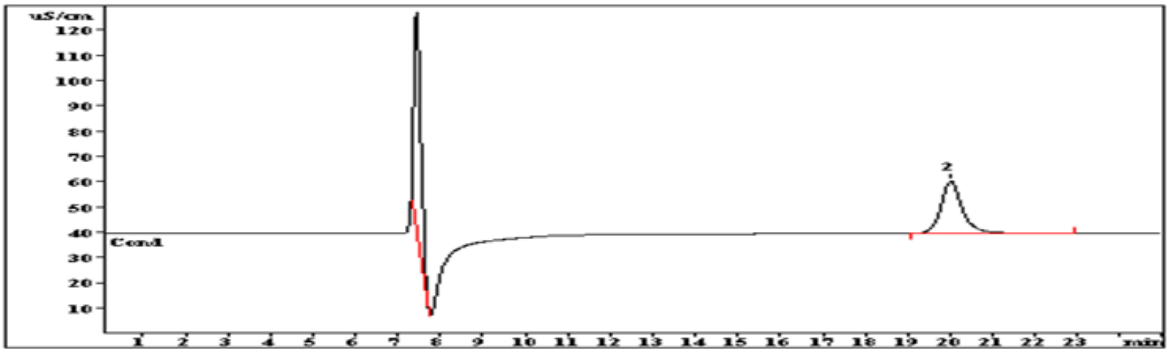


Figure 4.31: Chromatograms of CO_2 induced degradation products of D02PZ2M sample identified by OICM.

Table 4.25: Carbon dioxide induced degradation products of D02PZ2M identified by IC methods [Sample Code: D02PZ2M, Loading (α_L= 0.3, α_R = 0.8), pH (I) = 11.56, pH (F) = 8.05]

Analytical Method		DGPs and Details Parameters	
Analytical Method: IC	AICM	Peck Level (PL)	1, 2, 3, 4, 5, 6, 7
		DGP (PL: 5)	NO_3^-
		[DGP], ppm	6.474
		Std. Verification	RT: 8.33
		Additional DGP, Fig. 5.5	[NO_2^-] = 4.390, RT-6.15
	CICM	Peck Level	1, 2, 3, 4, 5, 6
		DGP (PL: 3)	NH_4^+
		[DGP], ppm	0.515
		Std. Verification	RT-6.91
	OICM	Peck Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A

4.2.1.3 Variation of concentration of Identified DGPs of PZ+H_2O+CO_2 System

Figure 4.32 shows the variation of peak areas of identified Degradation Products of D01PZ1M and D02PZ2M. D01PZ1M shows two two ionic DGPs which are acetate and phosphate where as the concentration of acetate is greater than phosphate. The ionic DGPs of D02PZ2M are nitrate and ammonium. Nitrate relatively shows greater concentration than ammonium. The concentration of ionic DGPs of this syatem is increases with amine concentration.

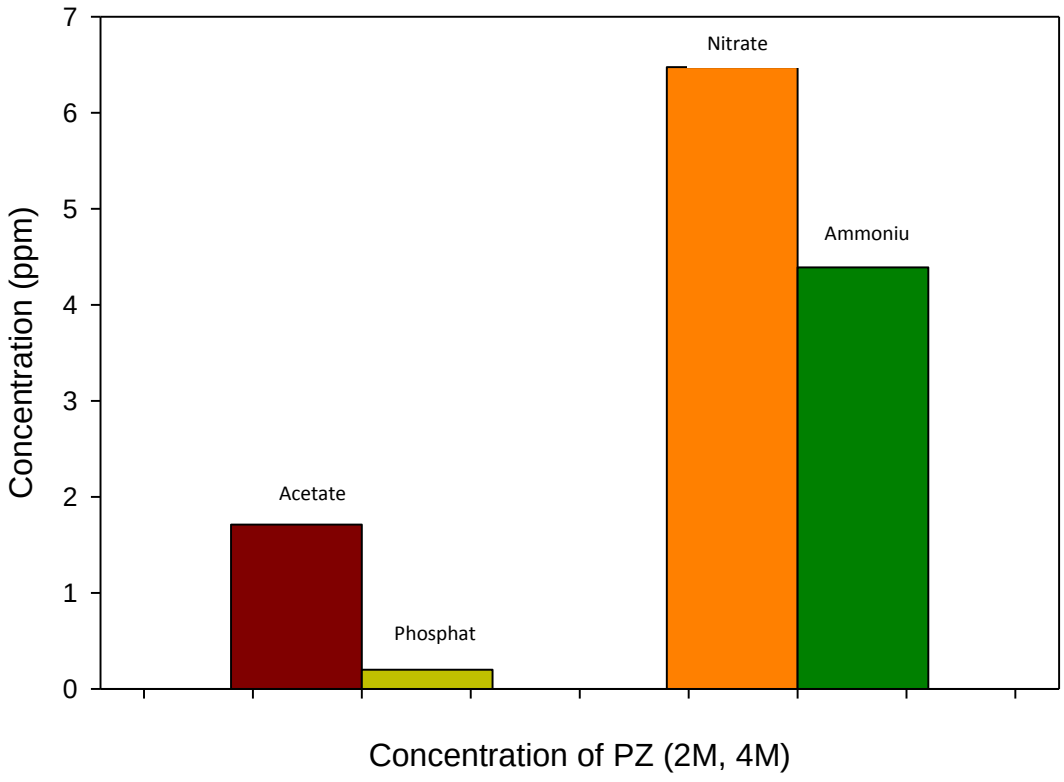


Figure 4.32: Variation of concentration of identified DGPs of D01PZ1M and D02PZ2M by IC methods

4.2.2 Degradation Products of DEA+H_2O+CO_2 System

In the following section the ionic degradation products of D03DEA2M, D04DEA3M and D05DEA4M are discussed for this degradation system. Three different IC methods are used in this detection.

4.2.2.1 Degradation Products of D03DEA2M

Table 4.21 gives details information for the sample D03DEA2M, its chromatogram of AICM is presented in figure 4.33. Two anionic degradation products i.e. nitrite and phosphate are detected in the chromatogram with concentration. The concentration of Nitrite and Phosphate ions are 643.19 and 882.00 ppm respectively. Phosphate and Nitrite are the typical ionic degradation products. The results are in accordance with that of provided that the condition of degradation in the work of Stewart and lanning are the same as this work (Stewart and Lanning, 1994). Samples are also analyzed by CICM and OICM however in both analyses no significant degradation was found these are shown by the figures 4.34 and 4.35 respectively. In CICM three pecks are observed but no one is detected. The overall degradation result of this sample D03DEA2M is given in table 4.26. The other possible reson can be mentioned that PZ is known as a noble solvent for its high stability up to 150 ˚C (Freeman, 2010). Hence it is assumed that no more degradation product is occurred under the experimental temperature100 ˚C in this work.

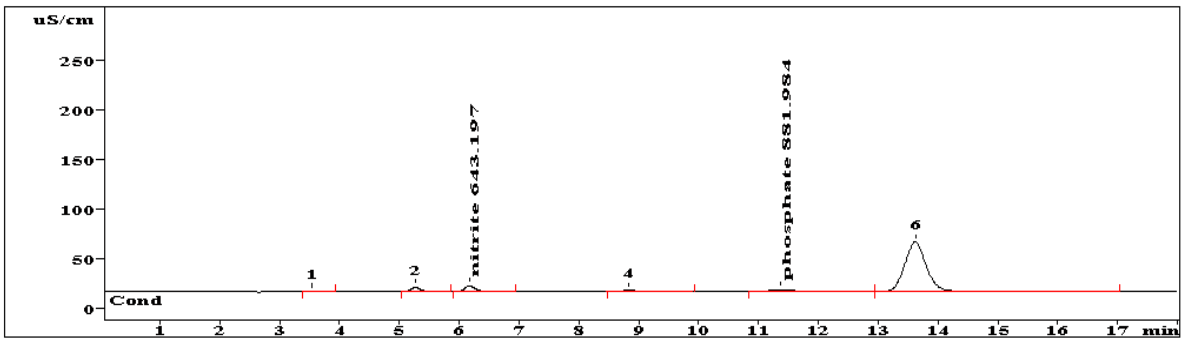


Figure 4.33: Chromatogram of carbon dioxide induced degradation products of D03DEA2M identified by anionic ion chromatographic method (AICM).

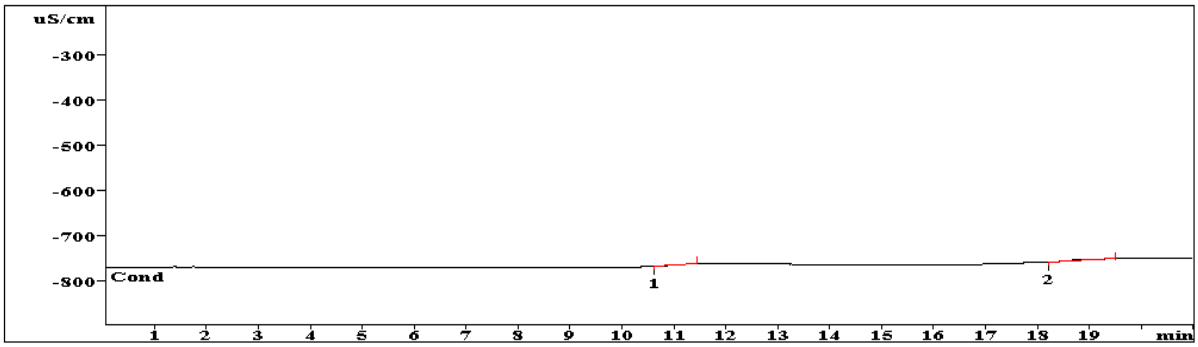


Figure 4.34: Chromatogram of carbon dioxide induced degradation products of D03DEA2M identified by cationic ion chromatographic method (CICM).

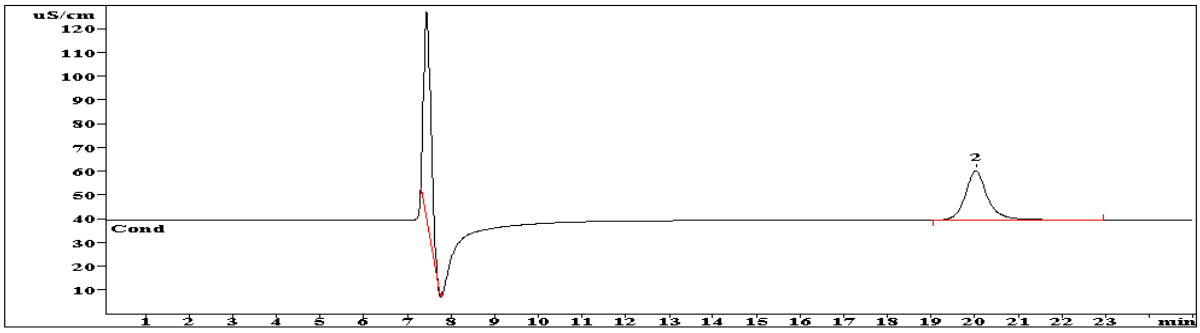


Figure 4.35: Chromatogram of carbon dioxide induced degradation products of D03DEA2M identified by organic acid ion chromatographic method (OICM).

Table 4.26: Carbon dioxide induced degradation products of D03DEA2M identified by IC methods [Loading (α_L= 0.28, α_R = 0.58), pH (I) = 10.11, pH (F) = 8.05]

Experiment and Analysis		**DGPs and Details Parameters**	
Analytical Method: IC	**AICM**	Peck Level (PL)	1, 2, 3, 4, 5
		DGP (PL: 3, 5)	NO_2^-, PO_4^{3-}
		[DGP], ppm	643.19, 882
		Std. Verification	RT: 6.3, 11.5
	CICM	Peck Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A
	OICM	Peck Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A

4.2.2.2 Degradation Products of D04DEA3M

The identified cationic degradation product of D04DEA3M is ammonium. The concentration of ammonium ion shown in figure 4.36, the results are in accordance with the work of Kadner (1999) and also supported in work of many researchers (M. Kaminski, 2002; O. Mrklas, 2003; Stewart and Lanning, 1994; Closmann et al., 2009). In the AICM the chromatogram shows six peaks, among these peaks three are identified which are acetate, nitrite and phosphate (Fig. 4.37). In OICM methods chromatograms showed two pecks (Fig. 4.38), however no one is detected. Table 4.27 summarizes the identified degradation products of D04DEA3M using IC methods and the identified DGP are acetate, nitrate, phosphate and ammonium.

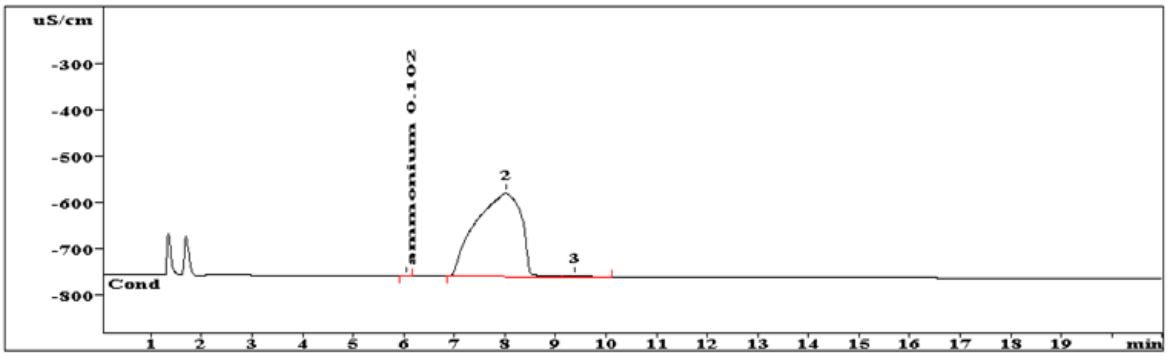


Figure 4.36: Chromatogram of carbon dioxide induced degradation products of D04DEA3M identified by cationic ion chromatographic method (CICM).

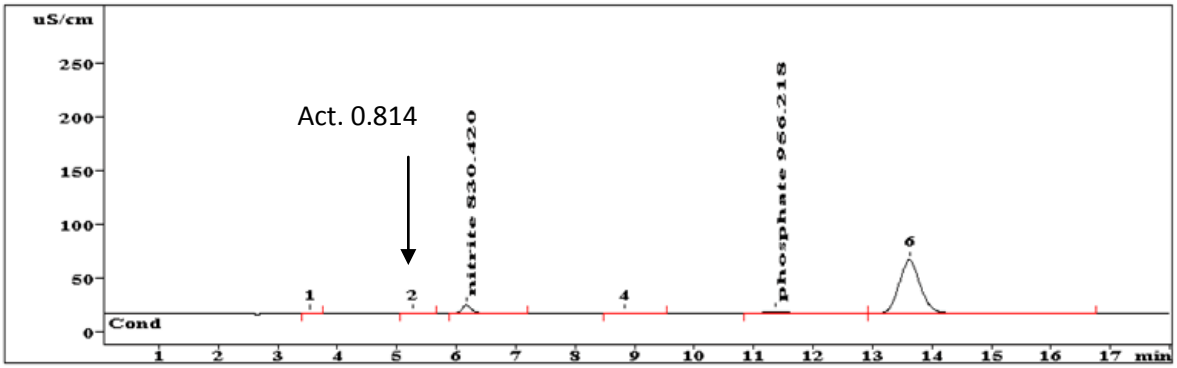


Figure 4.37: Chromatogram of carbon dioxide induced degradation products of D04DEA3M identified by anionic ion chromatographic method (AICM).

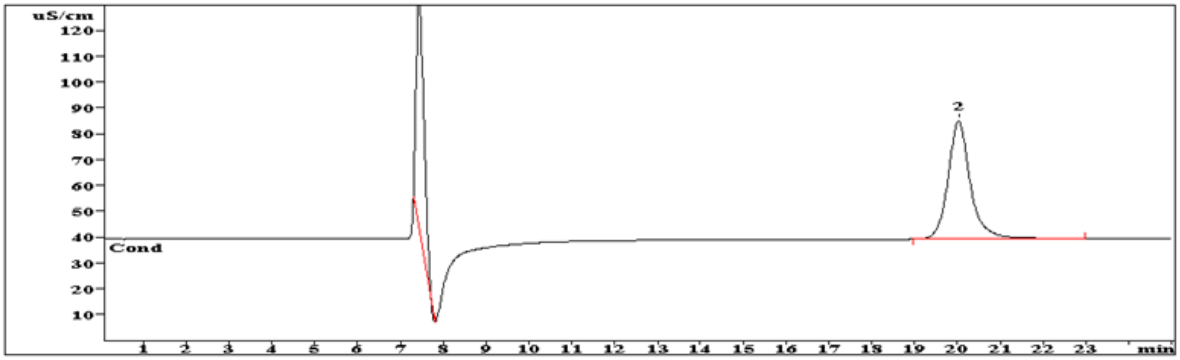


Figure 4.38: Chromatogram of carbon dioxide induced degradation products of D04DEA3M identified by organic acid ion chromatographic method (OICM).

Table 4.27: Carbon dioxide induced degradation products of D04DEA3M identified by IC method [Sample Code: D04DEA3M, Loading (α_L= 0.27, α_R = 0.56), pH (I) = 11.56, pH (F) = 8.05]

Experiment and Analysis	**DGPs and Details Parameters**		
Analytical method: IC	**AICM**	Peck Level (PL)	1, 2, 3, 4, 5, 6
		DGP (PL: 2, 3,5)	Act., NO_2^-, PO_4^{3-}
		[DGP], ppm	0.814, 830. 42, 956.22
		Std. Verification	RT: 4.09, 6.29, 11.5
	CICM	Peck Level	1, 2, 3
		DGP (PL: 1)	NH_4^+
		[DGP], ppm	0.102
		Std. Verification	RT-6.3
	OICM	Peck Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A

4.2.2.3 Degradation Products of D05DEA4M

The chromatogram of the DO5DEA4M samples from AICM analysis showed eight pecks, but only two are identified by this method, the detected degradation products are acetate and phosphate. The chromatograms of identified DGP are shown in the figure 4.39. The chromatogram of cationic IC method for DO5DEA4M sample shown in figure 4.40 which shows two peaks were as peak number one is identified. The identified DGP is ammonium which concentration and retention time was found 0.5 ppm and 6.303 min respectively. The consistency of this result is identical with many researchers in the open literature (Kadnar, 1999; O. Mrklas, 2003; M. Kaminski, 2002; Closmann et al., 2009). In the organic acid chromatographic methods the chromatograms showed two peaks but none is detected. The chromatogram of OICM for DO5DEA4M sample is given in the figure 4.41.

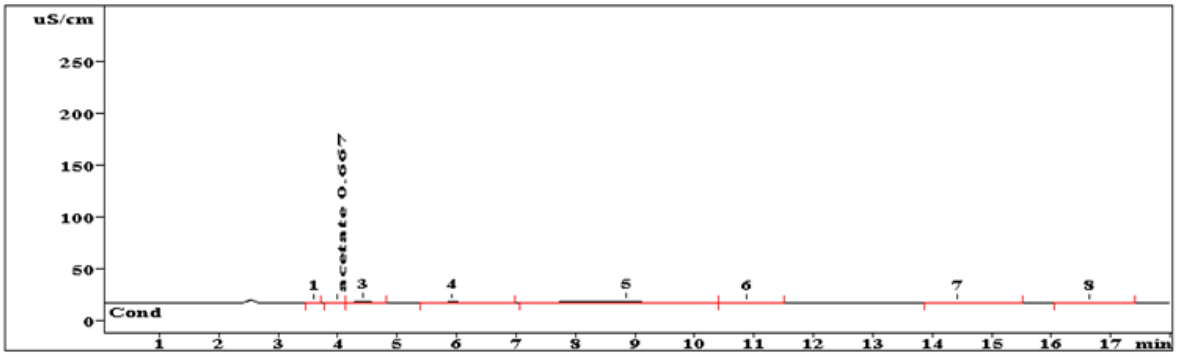


Figure 4.39: Chromatogram of carbon dioxide induced degradation products of DO5DEA4M identified by anionic ion chromatographic method (AICM).

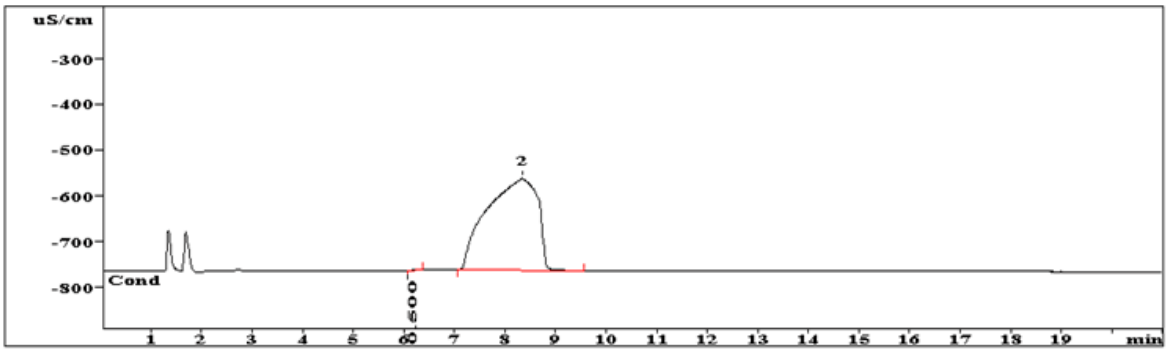


Figure 4.40: Chromatogram of carbon dioxide induced degradation products of DO5DEA4M identified by cationic ion chromatographic method (CICM).

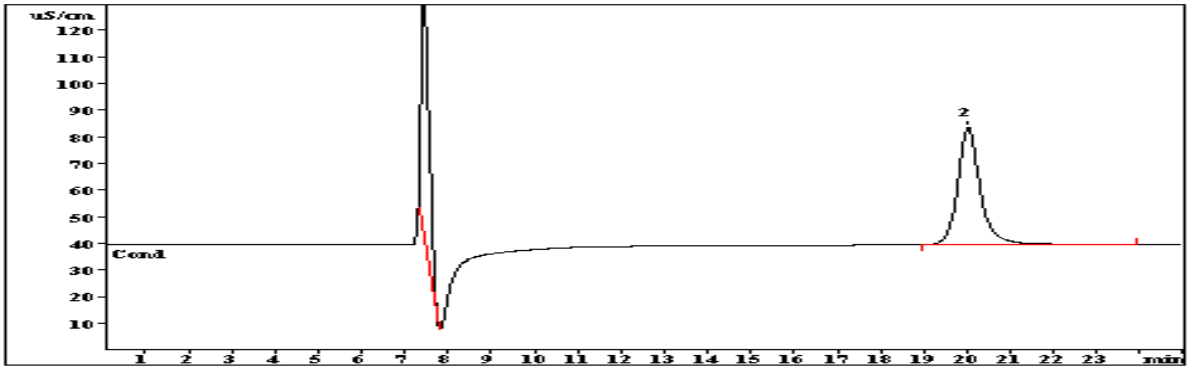


Figure 4.41: Chromatogram of carbon dioxide induced degradation products of DO5DEA4M identified by organic acid ion chromatographic method (OICM).

Amines are degraded and converted into alcohol, aldehyde and finally carboxylic acids. Even though higher molecular weight amines are degraded into lower molecular weight amine reported in the literature. MDEA degraded into DEA, later DEA degraded to MEA (Dawodu and Meisen, 1996). An insight to path of amine degradation was reported by Ronney which as shown in the reaction scheme D, Figure 4.42 (Rooney and Daniels, 1998). Table 4.28 summarizes identified degradation products by the IC methods.

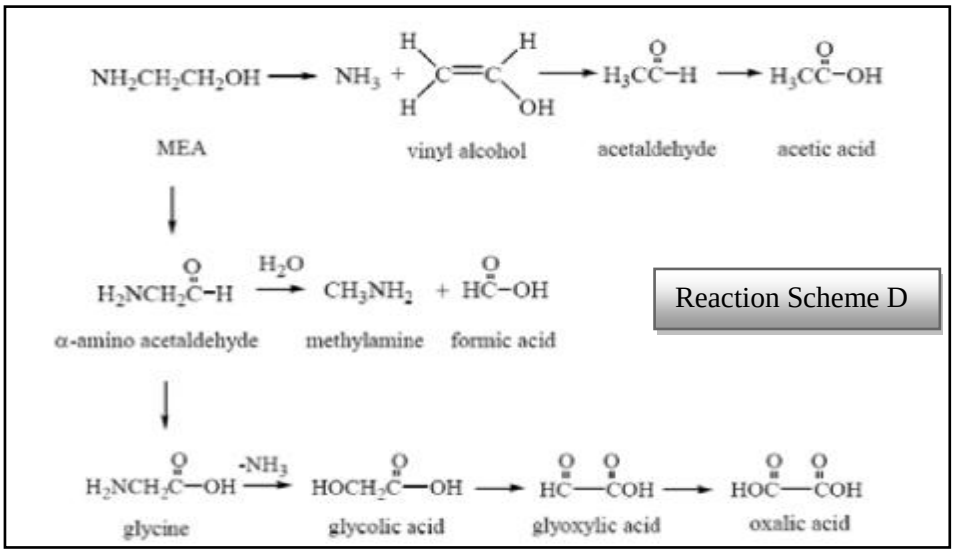


Figure 4.42: Reaction pathways for the formation acids, aldehyde and ketone from alkanolamine

Table 4.28: Carbon dioxide induced degradation products of D05DEA4M identified by IC methods [Loading (α_L= 0.34, α_R = 0.59), pH (I) = 9.76, pH (F) = 9.47]

Experiment and Analysis		DGPs and Details Parameters	
Analytical Method: IC	AICM	Peck Level (PL)	1-8
		DGP (PL: 1, 2)	Act, PO_4^{3-}
		[DGP], ppm	0.667, 2.524
		Std. Verification	RT: 4.09, 6.29,
	CICM	Peck Level	1, 2
		DGP (PL: 1)	NH_4^+
		[DGP], ppm	0.5
		Std. Verification	RT-6.303
	OICM	Peck Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A

4.2.2.4 Variation of Concentration of Ionic DGPs of DEA+H_2O+CO_2 System

Figure 4.43 represents the variation of concentration of ionic degradation products of D03DEA2M, D04DEA3M and D05DEA4M. Nitrite and Phosphate are the common ionic DGPs of D03DEA2M and D04DEA3M. The DGPs of D05DEA4M are acetate, ammonium and phosphate which are found very low concentration that's why these are not visible in the graphical diagram. The concentration of Nitrite and Phosphate are increases with amine concentration. The variation of concentration of identified DGPs for D05DEA4M does not follow any trend with alkanolamine concentration.

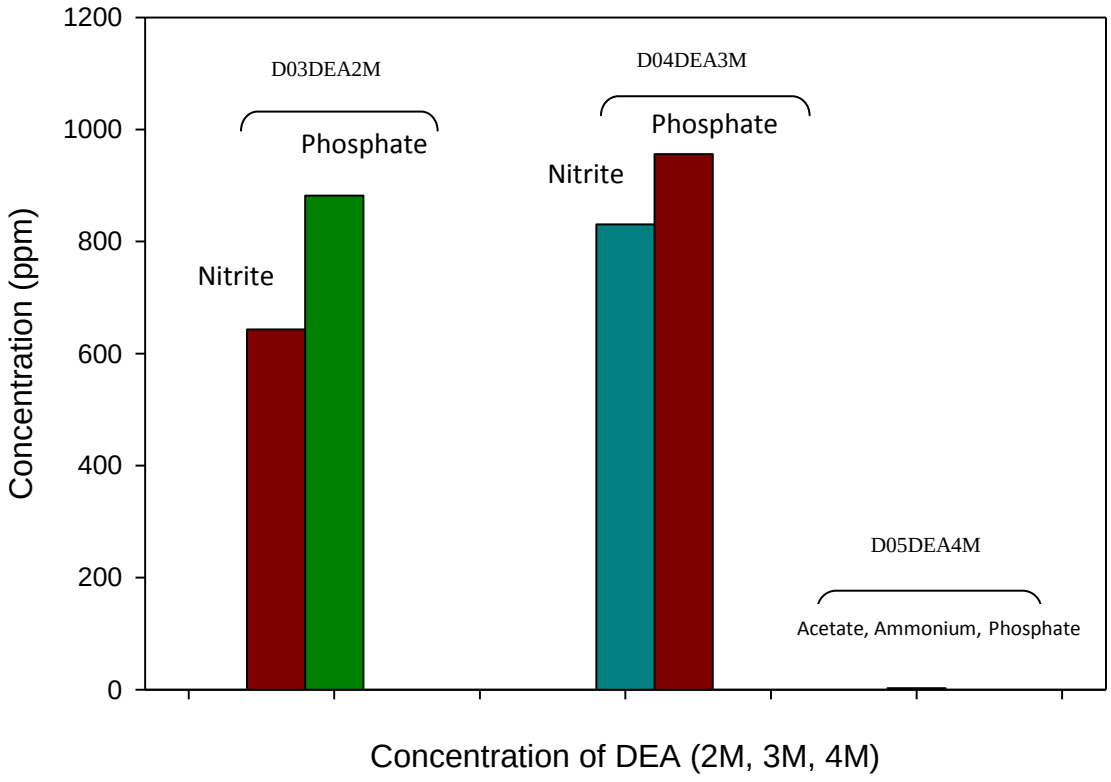


Figure 4.43: Variation of concentration of identified DGPs of D03DEA2M, D04DEA3M and D05DEA4M

4.2.3 Degradation Products of DEA+PZ+H_2O+CO_2 System

Five different concentrations of degraded activated DEA samples D06DEA2MPZ1M, D07DEA2MPZ2M, D08DEA3MPZ2M, D09DEA4MPZ2M and D10DEA7MPZ2M were analyzed by IC and the results are discussed in the following section.

4.2.3.1 Degradation Products of D06DEA2MPZ1M

The anionic ion chromatographic method (AICM) nitrite is identified, its chromatogram is shown in figure 4.44 where as two peaks are observed. Peak number one is detected and number two is unidentified. On the other hand figure 4.45 shows the chromatogram of CICM method for D06DEA2MPZ1M sample, two peaks are observed and one is detected. It is assume that the unknown peaks are protonated PZ or protonated DEA. Analysis is carried out for the sample using organic acid ion chromatographic method, illustrated in the figure 4.46 showed two peaks which are not identified. According to the IC standard information it is believed that it is most probably due to the butyrate ion.

The results are summarized in table 4.29. Based on the results it could be reported that activated DEA degraded slowly than inactivated DEA solution. Nitrite is the only identified DGP of this sample. Sexton et al., (2010) conducted an experiment on the degradation behavior of PZ (2.5M) at 55 ˚C induced by CO_2 and O_2 gas mixture and found NO_2^- radical as DGP by IC analysis which is identical with this present work (Sexton and Rochelle, 2010).

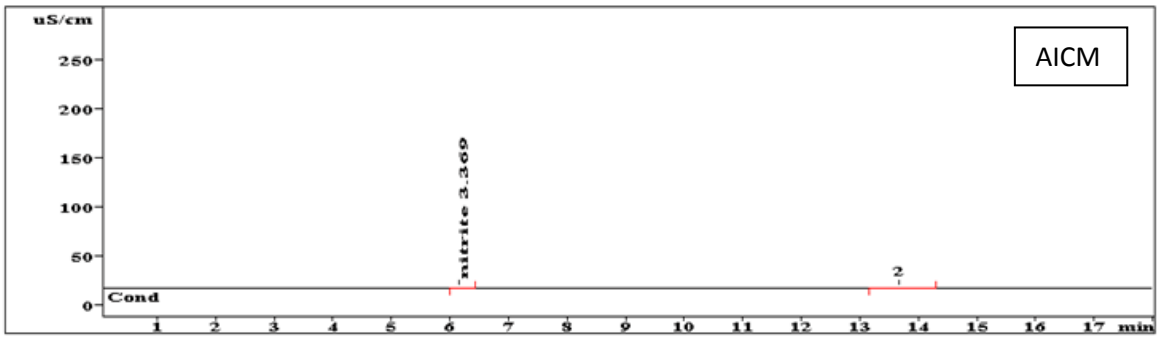


Figure 4.44: Chromatograms of carbon dioxide induced degradation of D06DEA2MPZ1M identified by AICM.

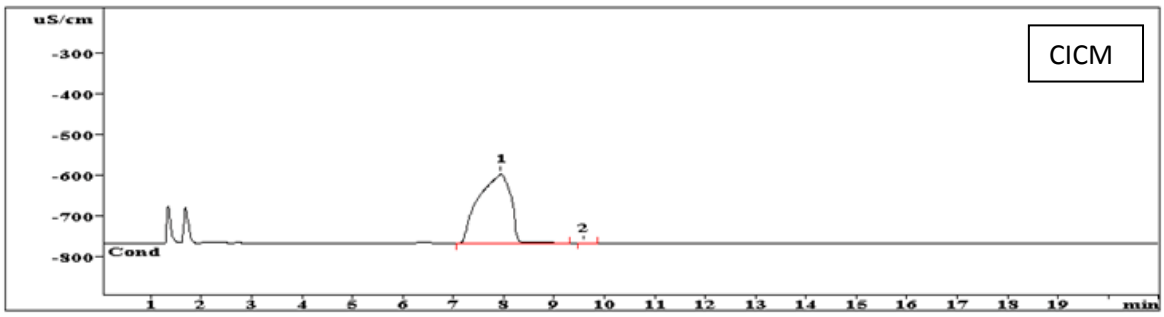


Figure 4.45: Chromatograms of carbon dioxide induced degradation of aqueous D06DEA2MPZ1M identified by CICM.

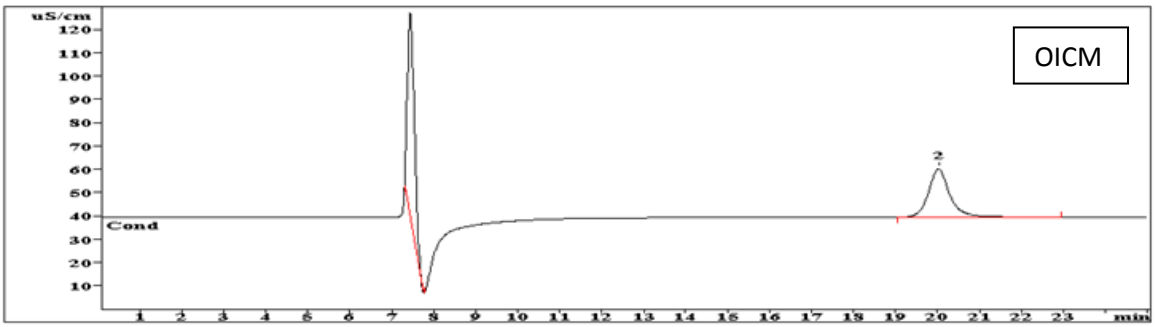


Figure 4.46: Chromatograms of carbon dioxide induced degradation of D06DEA2MPZ1M identified by OICM.

Table 4.29: Carbon dioxide induced degradation products of D06DEA2MPZ1M identified by IC analysis [Loading (α_L= 0.4, α_R = 0.7), pH (I) = 9.76, pH (F) = 9.47]

Experiment and Analysis		DGPs and Details Parameters	
Analytical Method: IC	AICM	Peck Level (PL)	1, 2
		DGP (PL: 1)	NO_2^-
		[DGP], ppm	3.369
		Std. Verification	RT: 6.15
	CICM	Peck Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A
	OICM	Peck Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A

4.2.3.2 Degradation Products of D07DEA2MPZ2M

The chromatogram of anion ion chromatographic method (AICM) for D07DEA2MPZ2M is shown in figure 4.47. Six peaks are observed and peak number three and five are identified which are nitrite and phosphate respectively. The chromatogram from cationic ion chromatographic method (CICM) of D07DEA2MPZ2M is shown in figure 4.48. Peak number two is identified as ammonium ion in the chromatogram and the other peaks are unknown. Figure 4.49 shows the chromatogram of organic acid ion chromatographic methods for D07DEA2MPZ2M, two peaks are observed but none of them is identified. It is most probably due to the presence of butyrate radical. The overall results from three IC methods for D07DEA2MPZ2M are summarized in Table 4.30. Nitrite, phosphate and ammonium are detected as degradation products. Amines are oxidized into nitrate and nitrite in the presence of oxygen, similar results were reported by Sexton and Rochelle (2010) while for the appearance of PO_4^{3-} in this work is believed to be due to the oxygen in gas into the experiment identified by Kadnar (Kadnar, 1999).

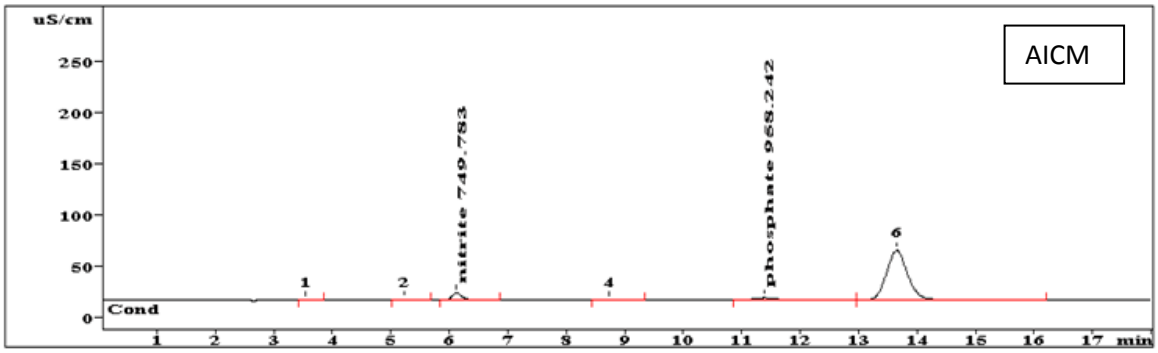


Figure 4.47: Chromatograms of carbon dioxide induced degradation of D07DEA2MPZ2M identified by AICM.

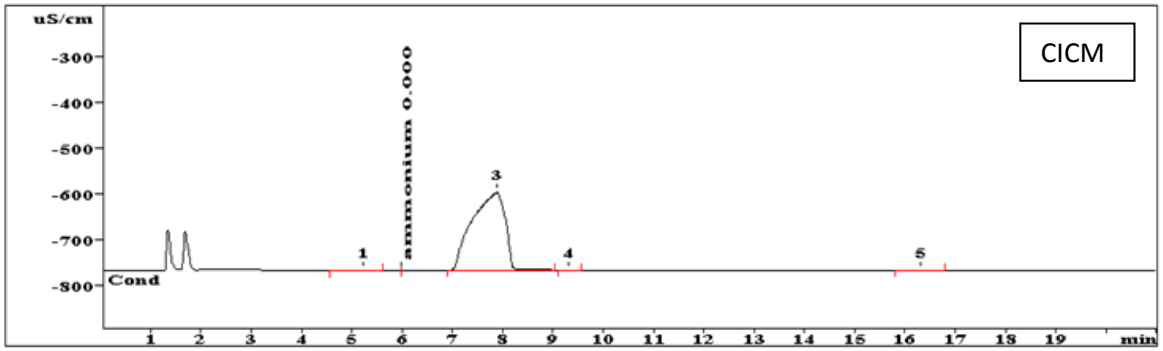


Figure 4.48: Chromatograms of carbon dioxide induced degradation of D07DEA2MPZ2M identified by CICM.

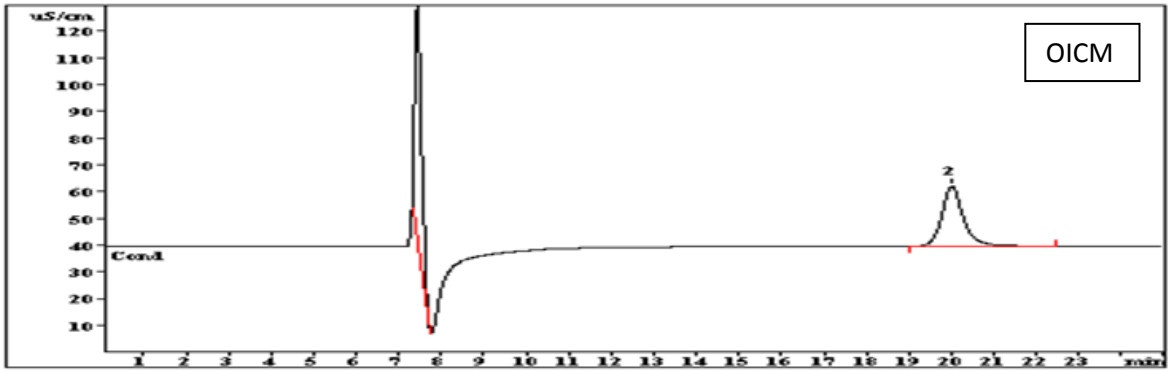


Figure 4.49: Chromatograms of carbon dioxide induced degradation of D07DEA2MPZ2M identified by OICM.

Table 4.30: Carbon dioxide induced degradation products of D07DEA2MPZ2M identified by IC method [Loading (α_L= 0.3, α_R = 0.7), pH (I) = 9.76, pH (F) = 9.47]

Experiment and Analysis		DGPs and Details Parameters	
Analytical method: IC	AICM	Peck Level (PL)	1-6
		DGP (PL: 3, 5)	NO_2^- , PO_4^{3-}
		[DGP], ppm	749.783, 958.242
		Std. Verification	RT: 6.12, 11.39
	CICM	Peck Level	1-5
		DGP (PL: 2)	NH_4^+
		[DGP], ppm	0.0000000000 (VLT)
		Std. Verification	RT: 5.9
	OICM	Peck Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A

4.2.3.3 Degradation Products of D08DEA3MPZ2M

D08DEA3MPZ2M sample is analyzed by anionic ion chromatographic method (AICM) and its chromatogram is shown in figure 4.50.The chromatogram shows six and peaks numbers 3 and 5 are detected these are nitrite and phosphate respectively. The chromatogram of cation ion chromatographic method (CICM) for D08DEA3MPZ2M sample is shown in figure 4.51. In this chromatogram two peaks are observed and none of them is identified. It is believed that these two peaks are most probably due to the presence of ammonium radical or protonated piperazine or protonated diethanolamine. Amines are easily oxidized and produce various carboxylic acids such as acetic acid, formic acid, glycolic acid, butyric acid, propionic acid and butyric acid. In order to detect these carboxylic acids the degraded solution is analyzed using organic acid ion chromatography methods. Figure 4.52 shows the chromatogram of OICM for the sample, two peaks are observed and none is detected. Table 4.31 summarizes the results of D08DEA3MPZ2M for all the methods.

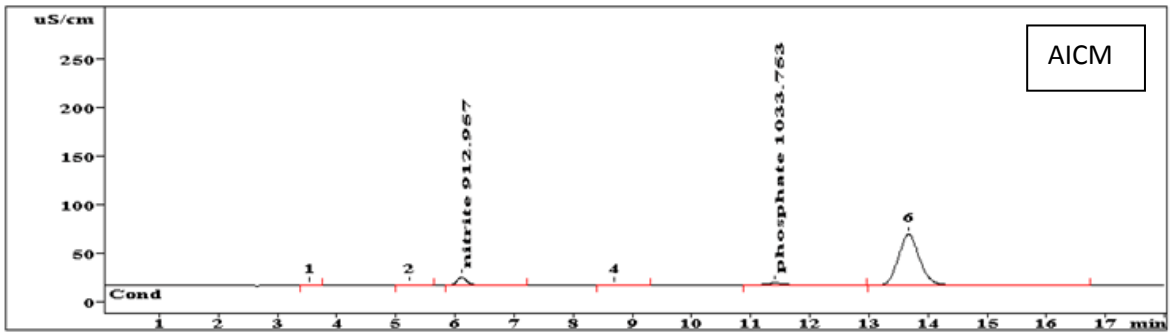


Figure 4.50 Chromatograms of carbon dioxide induced degradation of D08DEA3MPZ2M identified by AICM.

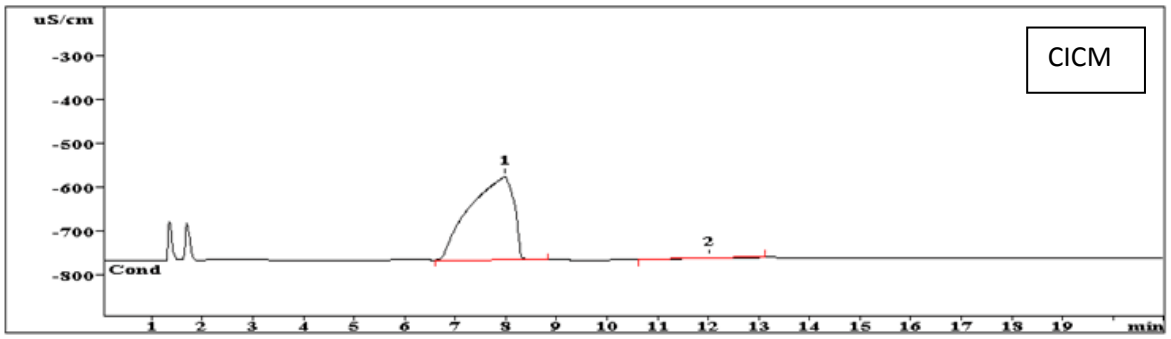


Figure 4.51: Chromatograms of carbon dioxide induced degradation of D08DEA3MPZ2M identified by CICM.

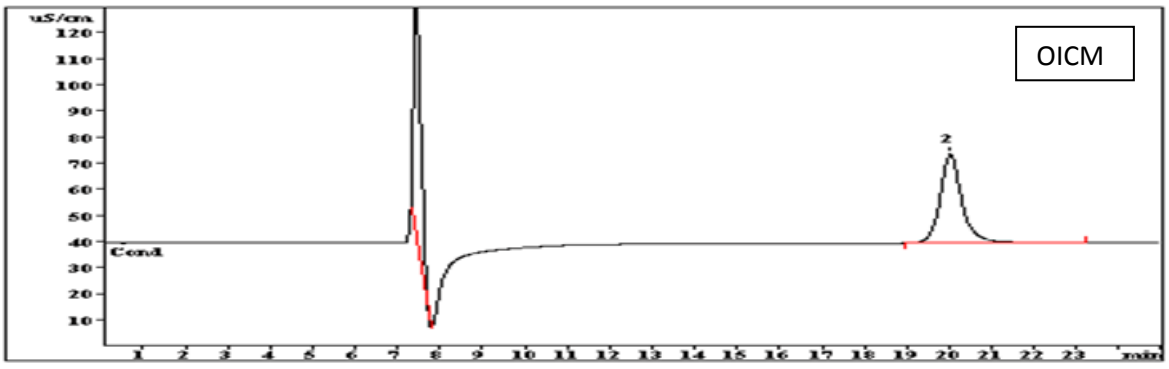


Figure 4.52: Chromatograms of carbon dioxide induced degradation of D08DEA3MPZ2M identified by OICM.

Table 4.31: Carbon dioxide induced degradation products of D08DEA3MPZ2M identified by IC methods [Loading (α_L= 0.32, α_R = 0.72), pH (I) = 9.76, pH (F) = 9.47]

Experiment and Analysis		DGPs and Details Parameters	
Analytical method: IC	AICM	Peck Level (PL)	1-6
		DGP (PL: 3, 5)	NO_2^- , PO_4^{3-}
		[DGP], ppm	912.967, 1033.763
		Std. Verification	RT: 6.11, 11.40
	CICM	Peck Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A
	OICM	Peck Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A

4.2.3.4 Degradation Products of D09DEA4MPZ2M

In anionic ion chromatographic method (AICM) nitrite is identified for D09DEA4MPZ2M and its chromatogram is shown in figure 4.53. Two peaks are observed in this chromatogram, peak number one is detected and peak number two is not. Cationic IC methods the chromatogram of D09DEA4MPZ2M showed two pecks, peaks number one is identified which is ammonium and two is not. Figure 4.54 presents the sample chromatogram. The result is in accordance with that found in the work of many researchers (Kadnar, 1999; O. Mrklas, 2003; M. Kaminski, 2002; Closmann et al., 2009). D09DEA4MPZ2M is analyzed using organic acid ion chromatographic method (OICM) and its chromatogram is shown in figure 4.55. Two peaks in the observed in the chromatogram but none is detected. AICM and CICM identified degradation products are nitrite and ammonium respectively while for OICM method no DGP was detected. Table 4.32 presents the details information of DGP using IC for D09DEA4MPZ2M.

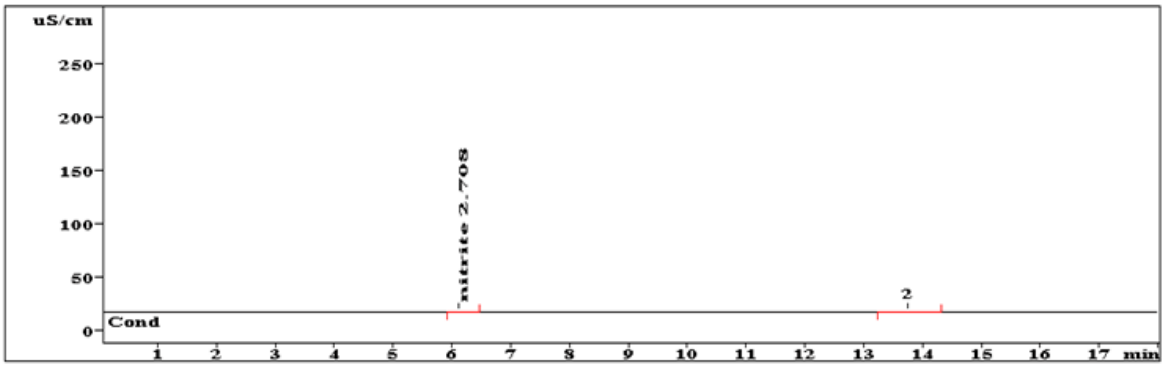


Figure 4.53: Chromatograms of carbon dioxide induced degradation of D09DEA4MPZ2M identified by AICM.

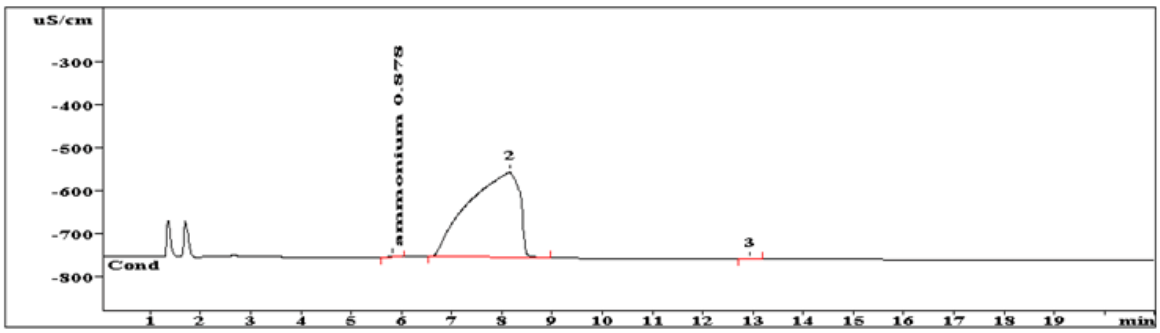


Figure 4.54: Chromatograms of carbon dioxide induced degradation of D09DEA4MPZ2M identified by CICM.

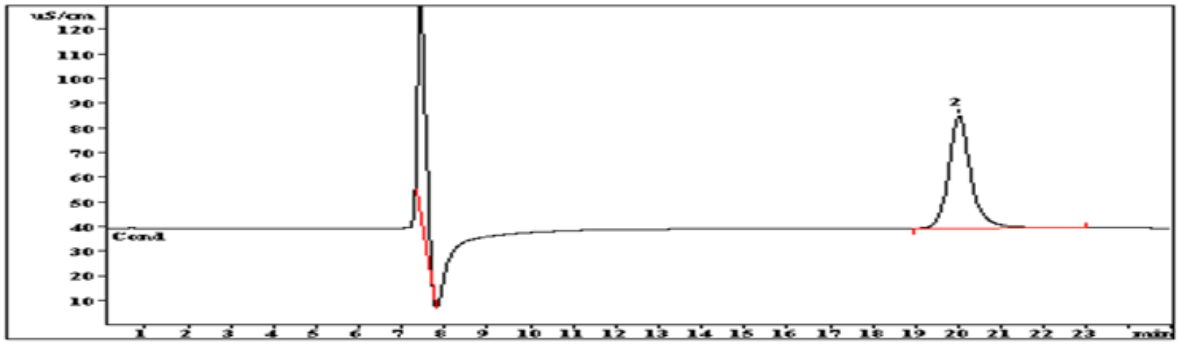


Figure 4.55: Chromatograms of carbon dioxide induced degradation of D09DEA4MPZ2M identified by OICM.

Table 4.32: Carbon dioxide induced degradation products of D09DEA4MPZ2M identified by IC methods [Loading (α_L= 0.3, α_R = 0.71), pH (I) = 9.76, pH (F) = 9.47]

Experiment and Analysis		DGPs and Details Parameters	
Analytical Method: IC	AICM	Peck Level (PL)	1-6
		DGP (PL: 1)	NO_2^-
		[DGP], ppm	2.708
		Std. Verification	RT: 6.09
	CICM	Peck Level	1, 2, 3
		DGP (PL: 1)	NH_4^+
		[DGP], ppm	0.878
		Std. Verification	RT: 5.83
	OICM	Peck Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A

4.2.3.5 Degradation Products of D10DEA7MPZ2M

The chromatogram of AICM for D10DEA7MPZ2M is shown in figure 4.56. There are six peaks found and peak number 2, 3 and 4 are identified, which are nitrite, nitrate and phosphate respectively. Figure 4.57 shows the chromatograms of D10DEA7MPZ2M using CICM method, there is only one detected peak between three which is ammonium. Similar results were reported by many researchers (Kadnar, 1999; O. Mrklas, 2003; M. Kaminski, 2002; Closmann et al., 2009). OICM method is used for D10DEA7MPZ2M and its chromatogram is shown in figure 4.58, there are two observed peaks and both are unknown. Based on the analysis it is assumed that peak number two is due to the presence of butyric acid. The details information of identified peaks and detected DGPs are given in the Table 4.33. The identified degradation products are nitrate, nitrite, phosphate and ammonium.

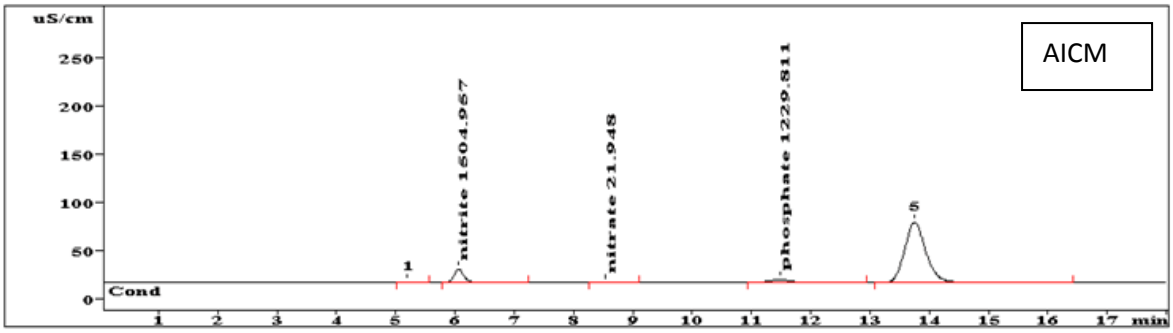


Figure 4.56: Chromatograms of carbon dioxide induced degradation of D10DEA7MPZ2M identified by AICM.

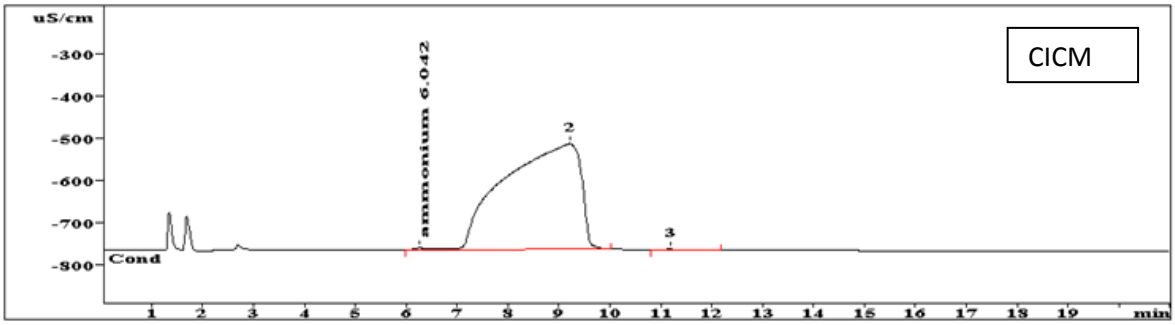


Figure 4.57: Chromatograms of carbon dioxide induced degradation of D10DEA7MPZ2M identified by CICM.

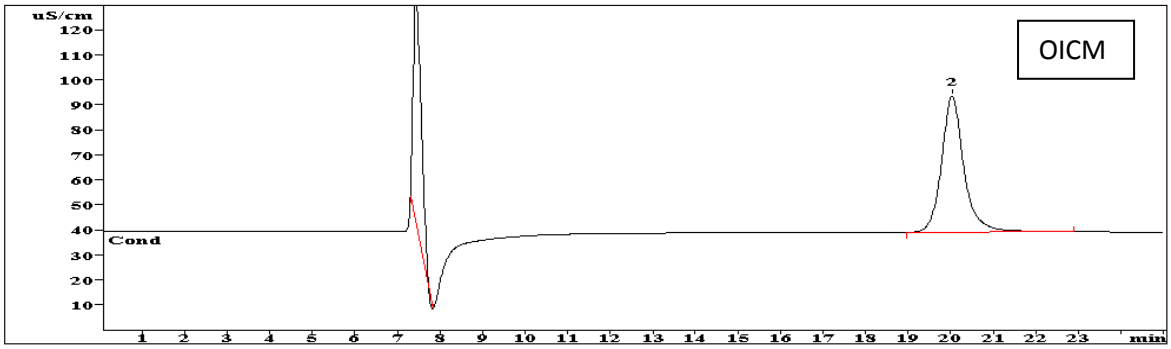


Figure 4.58: Chromatograms of carbon dioxide induced degradation of D10DEA7MPZ2M identified by OICM.

Table 4.33: Carbon dioxide induced degradation products of D10DEA7MPZ2M identified by IC method [Loading (α_L= 0.30, α_R = 0.73), pH (I) = 9.76, pH (F) = 9.47]

Experiment and Analysis	DGPs and Details Parameters		
Analytical method: IC	AICM-01	Peck Level (PL)	1-5
		DGP (PL: 2, 3, 4)	NO_2^- , NO_3^-, PO_4^{3-}
		[DGP], ppm	1604.97, 21.95, 1229.81
		Std. Verification	RT: 6.05, 8.53, 11.47
	AICM-02	Peck Level (PL)	1-7
		DGP (PL: 3)	NO_2^-
		[DGP], ppm	1.581
		Std. Verification	RT: 6.17
	CICM	Peck Level	1, 2, 3
		DGP (PL: 1)	NH_4^+
		[DGP], ppm	6.042
		Std. Verification	RT: 6.26
	OICM	Peck Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A

4.2.3.6 Variation of Concentration of Ionic DGPs of DEA+PZ+H_2O+CO_2 System

The variation of concentration of ionic degradation products of D06DEA2MPZ1M and D09DEA4MPZ2M are shown in the Figure 4.59. The common degradation product of these two samples is nitrite and one additional product is obtained for D09DEA4MPZ2M which is ammonium. The concentration of nitrite ion is decreases with amine concentration and does not follow any trends which are clearly appeared in the following figure.

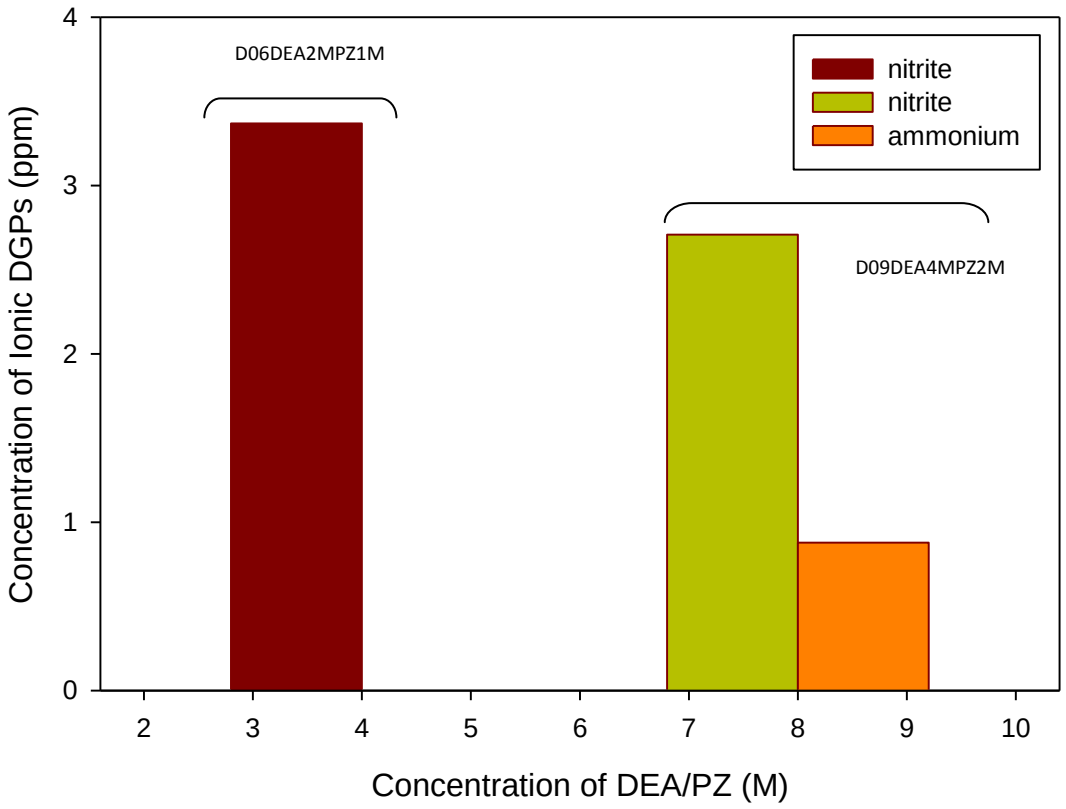


Figure 4.59: Variation of concentration of identified DGPs of D01PZ1M and D02PZ2M by IC methods

Figure 4.60 shows the variation of ionic DGPs concentration for D07DEA2MPZ2M, D08DEA3MPZ2M and D10DEA7MPZ2M. The common ionic DGPs for these thre samples are Nitrite and Phosphate which are increases with amine concentration. The sample D10DEA7MPZ2M shows two more ionic degtradation products which are ammonium and nitrate. In this figure Nitrite was found to occure highest concentration than others identified DGPs. On the other hand ammonium and mitrate are found to occupy very low concentration. Finally it could be concluded that the identified degradation producte nitrite and phosphate are found to follow trends with amine concentration but ammonium nd nitrate are randomly changed with amine concentration.

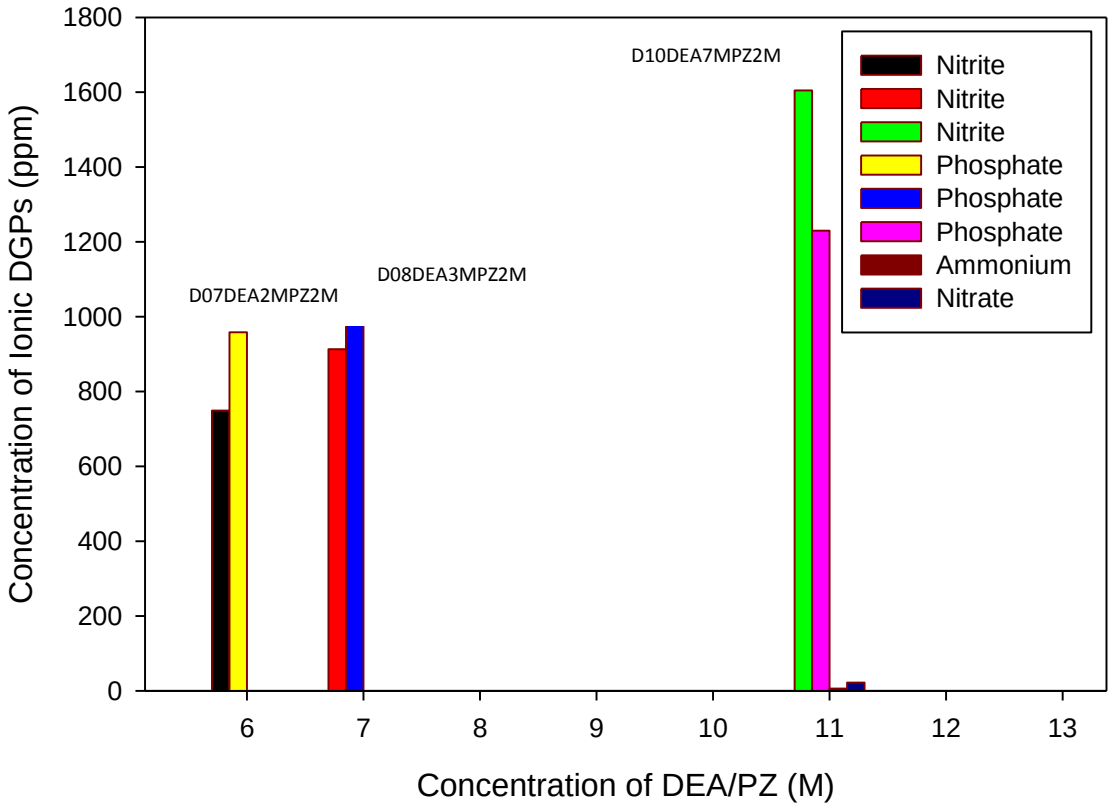


Figure 4.60: Variation of concentration of identified DGPs of D01PZ1M and D02PZ2M by IC methods

4.2.4 Degradation Products of MDEA+H_2O+CO_2 System

In order to characterize the ionic DGPs of D11MDEA2M, D12MDEA3M and D13MDEA4M are analyzed using IC methods. The results are discussed in the following section.

4.2.4.1 Degradation Products of D11MDEA2M

The chromatogram of AICM for D11MDEA2M is shown in figure 4.61, there are five peaks are observed in the chromatogram and peak number three and four are identified which are nitrite and phosphate. Since the presences of undetected peaks are many in figure 4.61, so in order to dtect these unknown peaks it is analyzed twice times by AICM and acetate is found as additional DGP with phosphate ion which shown in the figure 4.62. The chromatogram of CICM for D11MDEA2M is presented in figure 4.63, only one DGP was identified and the results are in accordance with that reported by many researchers (Kadnar, 1999; O. Mrklas, 2003; M. Kaminski, 2002; Closmann et al., 2009).

On the other hand, OICM analysis for D11MDEA2M is presented in figure 4.64, two peaks are observed and none of them is detected. Based on the result analysis and existing calibration standards it is assumed that peak number two is most probably due to the presence of butyric acid. Table 4.34 summarizes the results of IC analysis for the sample D11MDEA2M. The identified DGPs are ammonium, acetate, phosphate and nitrite.

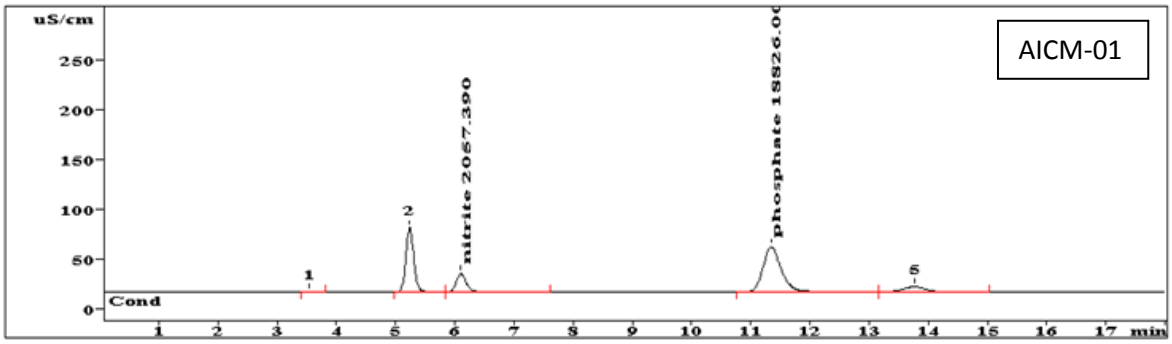


Figure 4.61: Chromatograms of carbon dioxide induced degradation of D11MDEA2M identified by AICM-01.

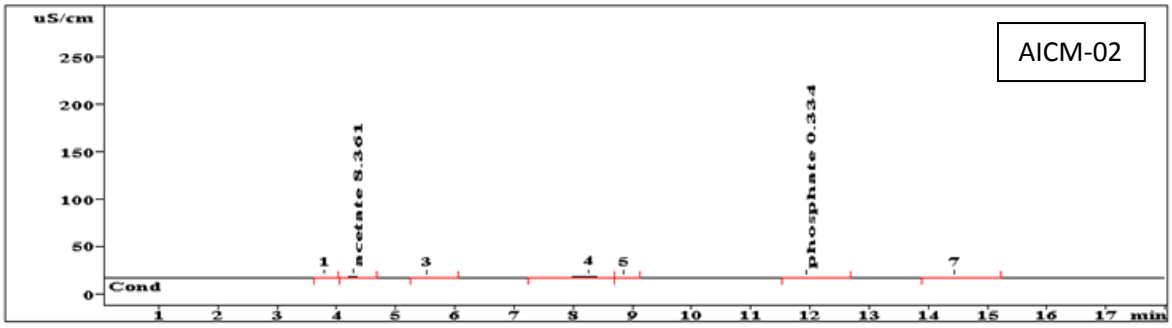


Figure 4.62: Chromatograms of carbon dioxide induced degradation of D11MDEA2M identified by AICM-02.

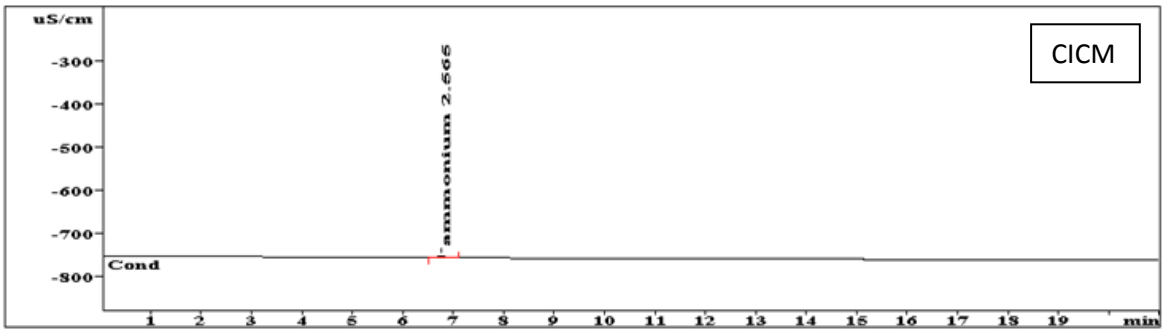


Figure 4.63: Chromatograms of carbon dioxide induced degradation of D11MDEA2M identified by CICM.

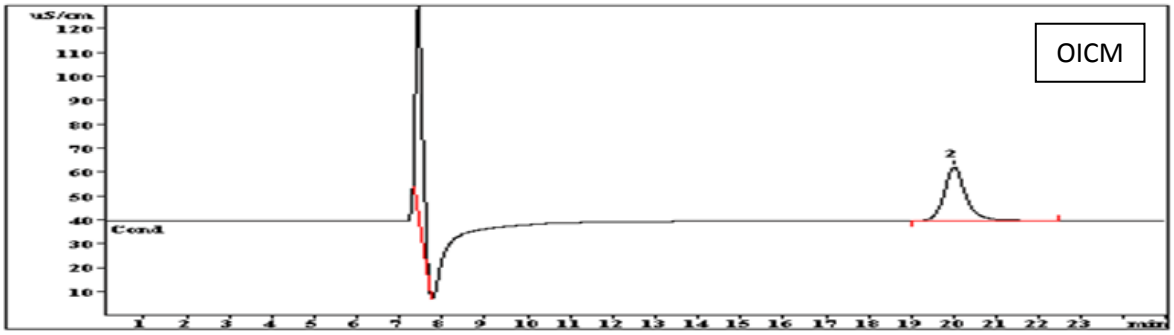


Figure 4.64: Chromatograms of carbon dioxide induced degradation of D11MDEA2M identified by OICM.

Table 4.34: List of carbon dioxide induced degradation products of D11MDEA2M identified by IC method [Loading (α_L= 0.10, α_R = 0.18), pH (I) = 9.76, pH (F) = 9.47]

Method		**DGPs and Details Parameters**	
Analytical method: IC	**AICM-01**	Peck Level (PL)	1-6
		DGP (PL: 3, 4)	NO_2^- , PO_4^{3-}
		[DGP], ppm	2067.390, 18826.00
		Std. Verification	RT: 6.09, 11.34
	AICM-02	Peck Level (PL)	1-7
		DGP (PL: 2, 6)	Act. , PO_4^{3-}
		[DGP], ppm	8.361, 0.334
		Std. Verification	RT: 4.27, 11.93
	CICM	Peck Level	1
		DGP (PL: 1)	NH_4^+
		[DGP], ppm	2.666
		Std. Verification	RT: 6.77
	OICM	Peck Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A

4.2.4.2 Degradation Products of D12MDEA3M

Figure 4.65 shows the chromatogram of D12MDEA3M, five peaks are observed and peak number three and six are identified which are nitrite and phosphate. The other remaining peaks are unknown. In order to detect unknown peaks in figure 4.65 the same sample (D12MDEA3M) is analyzed twice times and the chromatogram is shown in figure 4.66 with one additional degradation products which is acetate. The chromatogram of CICM of this sample is shown in figure 4.67 and three peaks are observed but none is detected. This is assumed that, peaks number one is due to the presence of ammonium species. Because the retention time of this peak is already identified as ammonium in case of D11MDEA2M sample. Rests of the peaks are still unknown and these are most probably due to the presence of protonated $MDEA^{+}$ or others amines. The chromatogram of OICM for D12MDEA3M is shown in the figure 4.68. Two peaks are observed in this chromatogram and both are unknown. Based on the data analysis and existing calibration standards it is assumed that peak no two is due to the presence of butyric acid. The solution has to be analyzed by HPLC or GC in order to get the absolute information regarding butyric acid or other unknown DGP. Table 4.35 summarizes the identified degradation products of D12MDEA3M these are acetate, nitrite and phosphate. The effects of these DGPs and consistancey of results are reported by many researchers (DOW, 2001; M. S.Islam, 2010; Carlson et al., 2001).

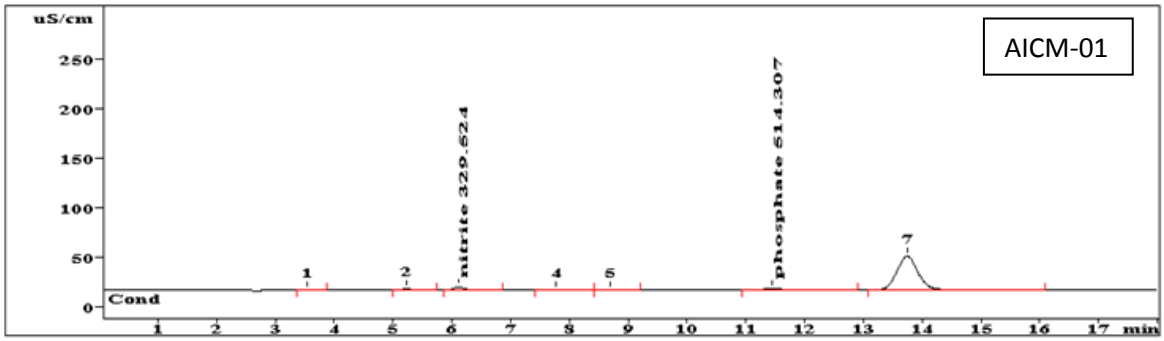


Figure 4.65: Chromatograms of carbon dioxide induced degradation of D12MDEA3M identified by AICM-01.

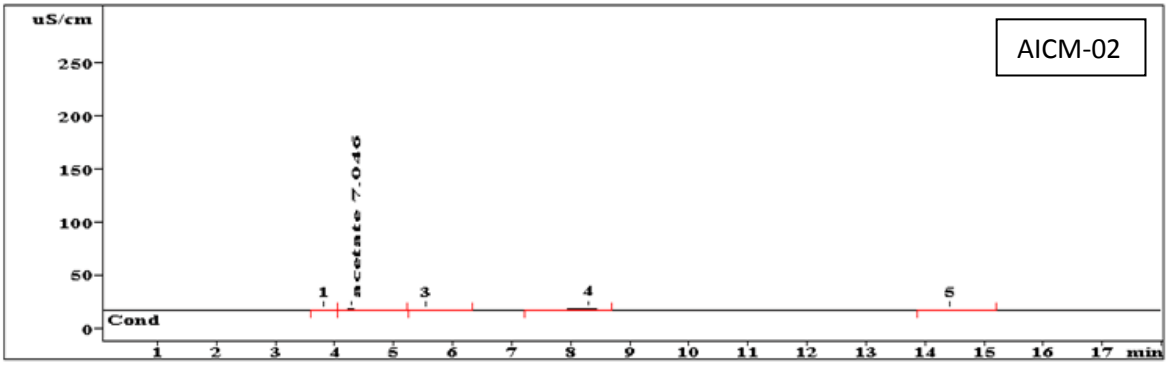


Figure 4.66: Chromatograms of carbon dioxide induced degradation of D12MDEA3M identified by AICM-02.

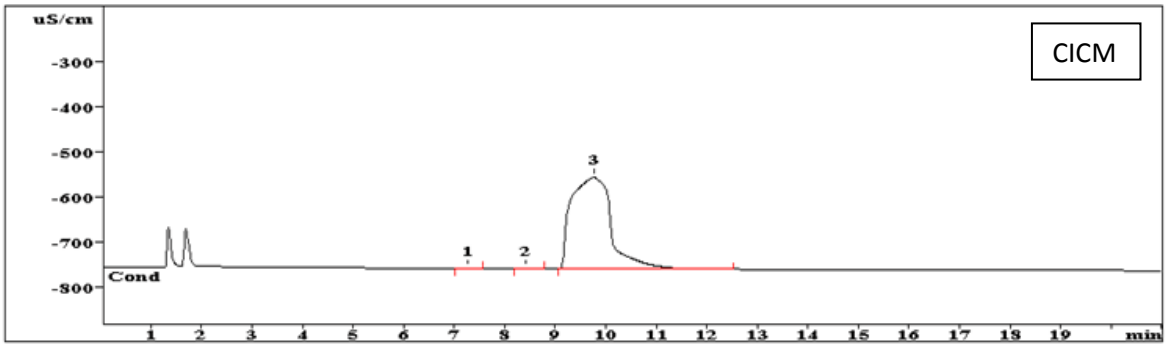


Figure 4.67: Chromatograms of carbon dioxide induced degradation of D12MDEA3M identified by CICM.

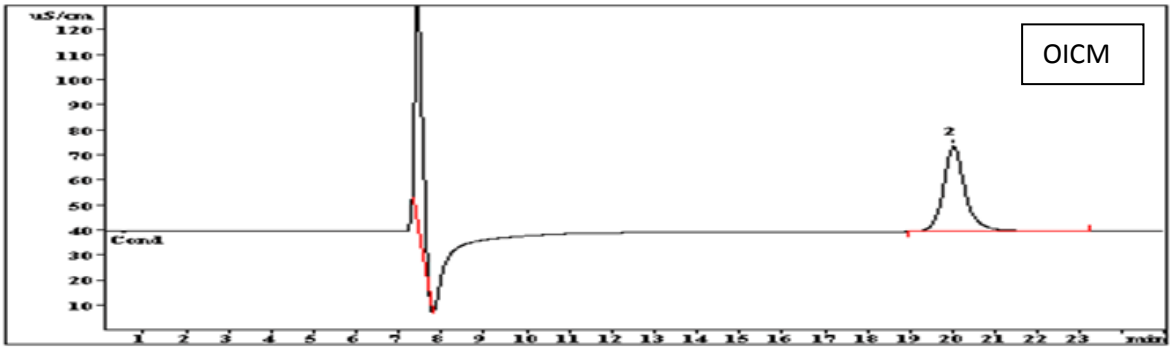


Figure 4.68: Chromatograms of carbon dioxide induced degradation of D12MDEA3M identified by OICM.

Table 4.35: List of carbon dioxide induced degradation products of D12MDEA3M identified by IC method [Loading (α_L= 0.1, α_R = 0.2), pH (I) = 9.76, pH (F) = 9.47]

Experiment and analysis		DGPs and Details Parameters	
Analytical method: IC	AICM-01	Peck Level (PL)	1-7
		DGP (PL: 3, 6)	NO_2^- , PO_4^{3-}
		[DGP], ppm	329.624, 614.307
		Std. Verification	RT: 6.10, 11.45
	AICM-02	Peck Level (PL)	1-6
		DGP (PL: 2)	Acetate
		[DGP], ppm	7.046
		Std. Verification	RT: 4.27
	CICM	Peck Level	1, 2, 3
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A
	OICM	Peck Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A

4.2.4.3 Degradation Products of D13MDEA4M

The chromatogram of AICM for D13MDEA4M sample is shown in the figure 4.69. Five peaks are observed in the chromatogram and peak number three and four are identified these are nitrite and phosphate. Figure 4.70 represents the chromatogram of CICM for D13MDEA4M which shows two peaks and none of them is detected. It is believed that these two unknown peaks are due to the presence of ammonium or protonated MDEA or other positively charged DGP. Chromatogram of organic acid ion chromatographic method (OICM) is shown in figure 4.71. Two peaks are observed in the chromatogram and both are unknown. Based on the results analysis and existing calibration standards it is assumed that peak number two is due to the presence of butyric acid. The identified degradation products of this sample (D13MDEA4M) are nitrite and phosphate and ammonium which is summarizes in the table 4.36.

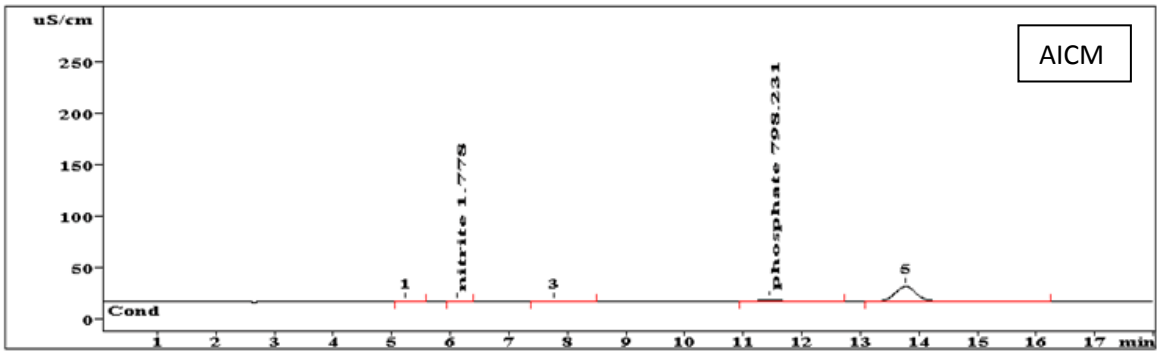


Figure 4.69: Chromatograms of carbon dioxide induced degradation of D13MDEA4M identified by AICM.

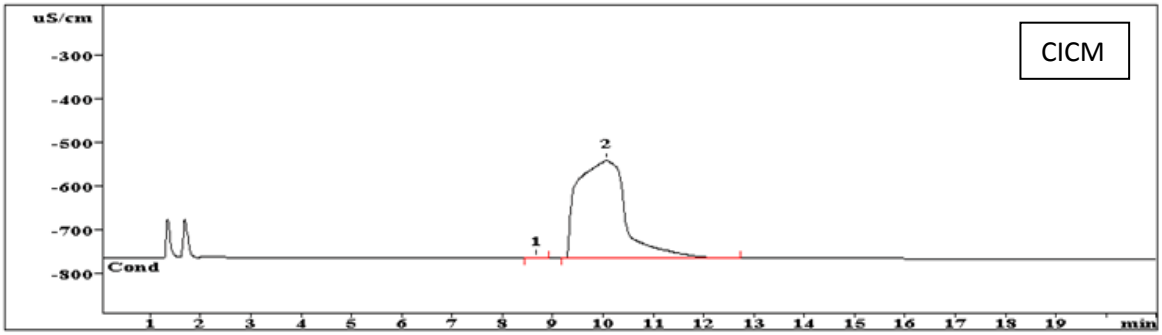


Figure 4.70: Chromatograms of carbon dioxide induced degradation of D13MDEA4M identified by CICM.

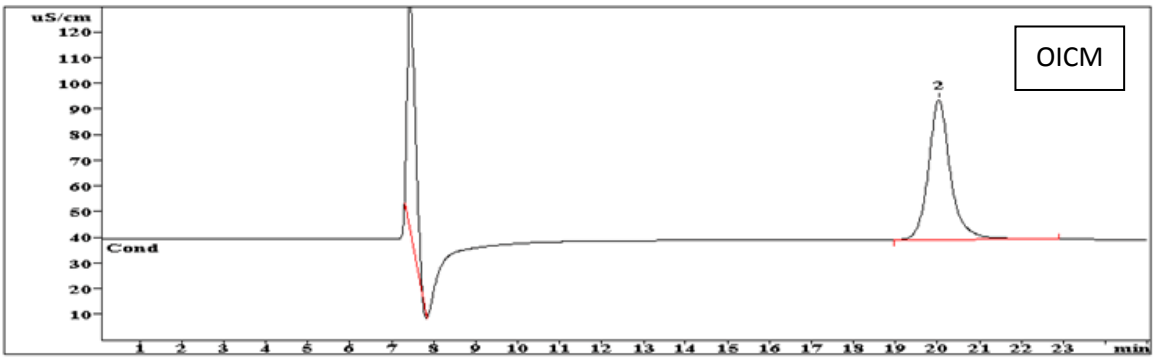


Figure 4.71: Chromatograms of carbon dioxide induced degradation of D13MDEA4M identified by OICM.

Table 4.36: List of carbon dioxide induced degradation products of D13MDEA4M identified by IC methods [Loading (α_L= 0.1, α_R = 0.2), pH (I) = 9.76, pH (F) = 9.47]

Sample		DGPs and Details Parameters	
Analytical method: IC	AICM	Peak's Level (PL)	1-6
		DGP (PL: 2, 4)	NO_2^-, PO_4^{3-}
		[DGP], ppm	1.778, 798.231
		Std. Verification	RT: 6.10, 11.45
	CICM	Peak's Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A
	OICM	Peak's Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A

4.2.4.4 Variation of Concentration of Ionic DGPs of MDEA+H_2O+CO_2 System

Figure 4.72 shows the variation of concentration of ionic degradation products of D11MDEA2M, D11MDEA2M and D11MDEA2M. Figure 4.72A shows the variation of acetate, ammonium and nitrite ions. On the other hand figure 4.72B shows the variation of concentration of nitrite and ohosphate ions. Among these degradation products nitrite and phosphate are found to occupy highest concentration. In case of D11MDEA2M and D11MDEA2M, the concentration of acetate, phosphate and nitrite are decreases with increasing of amine concentration. For D13MDEA4M, the concentration of phosphate is relatively increased than D12MDEA3M.

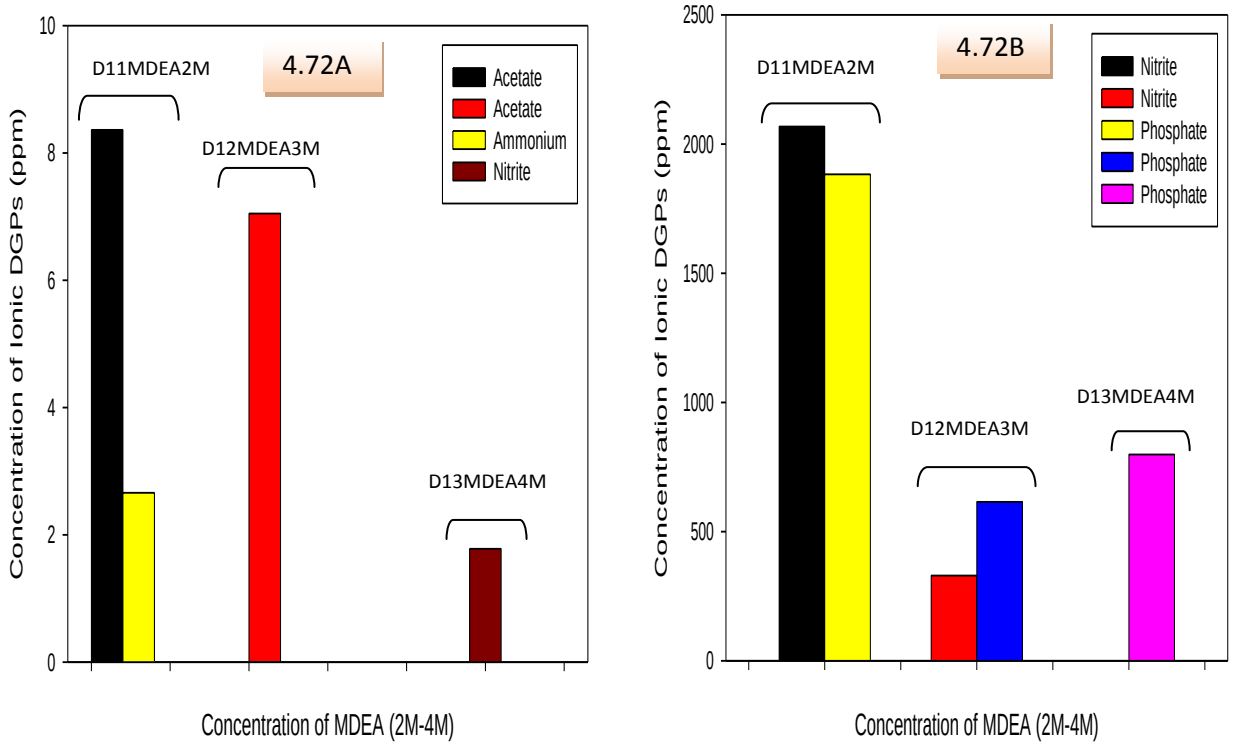


Figure 4.72: Variation of concentration of identified DGPs of D11MDEA2M, D11MDEA2M and D11MDEA2M.

4.2.5 Degradation Products of MDEA+PZ+H_2O+CO_2 System

Degraded MDEA solutions D14MDEA2MPZ1M, D15MDEA2MPZ2M, D16MDEA3MPZ2M, D17MDEA4MPZ2M and D18MDEA7MPZ2M are analyzed by IC methods and results are discussed in the following section.

4.2.5.1 Degradation Products of D14MDEA2MPZ1M

The chromatogram of AICM for D14MDEA2MPZ1M sample is shown in the figure 4.73. There are five peaks observed in the chromatogram and peak numbers 2, 3 and 4 are identified which are nitrite, nitrate and phosphate respectively. The chromatogram of CICM for D14MDEA2MPZ1M shown in the figure 4.74 which shows two peaks but none of them are detected. Peak number one is believed due to the presence of ammonium ion. The other peak is probably due to the presence of protonated PZ or MDEA. In order to investigate the presence of organic acids into this sample it is analyzed by organic acid ion chromatography method (OICM).

The chromatogram is shown in the figure 4.75 where as two peaks are observed and both peaks are unknown. Finally the identified degradation products of D14MDEA2MPZ1M using IC methods are nitrite, nitrate and phosphate which summarizes in the table 4.37. The effect of these DGPs and reliability of these results are reported in the open literature (DOW, 2001; M. S.Islam, 2010; Carlson et al., 2001).

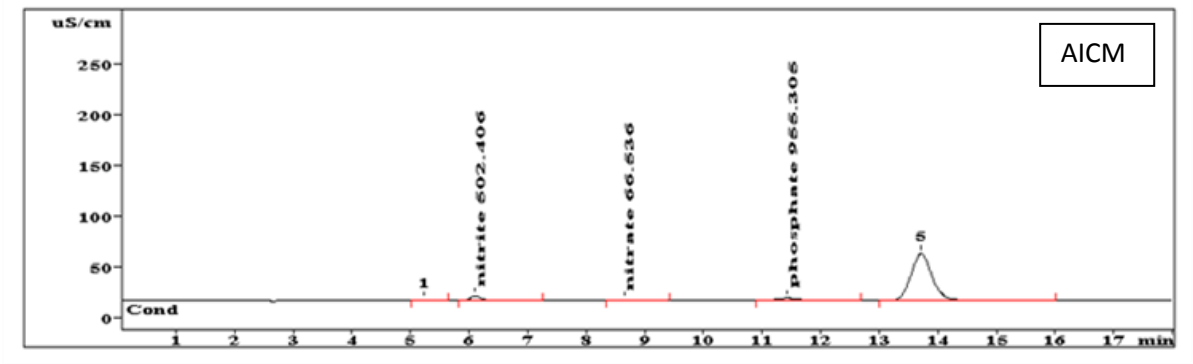


Figure 4.73: Chromatogram of carbon dioxide induced degradation of D14MDEA2MPZ1M identified by AICM.

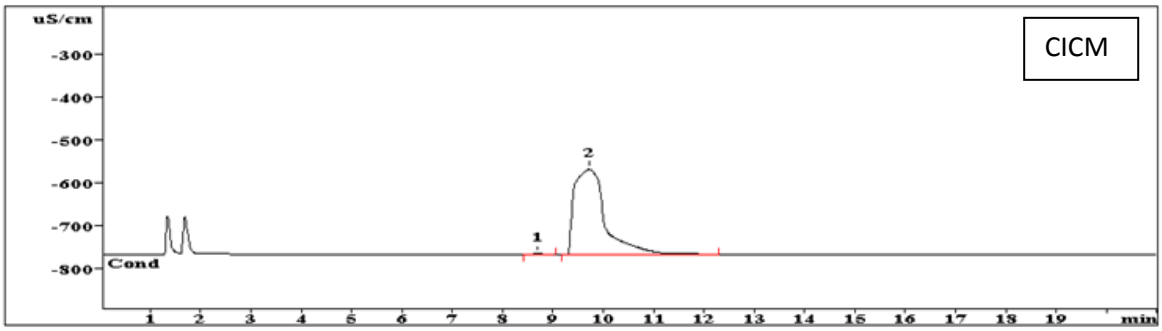


Figure 4.74: Chromatograms of carbon dioxide induced degradation of D14MDEA2MPZ1M identified by CICM.

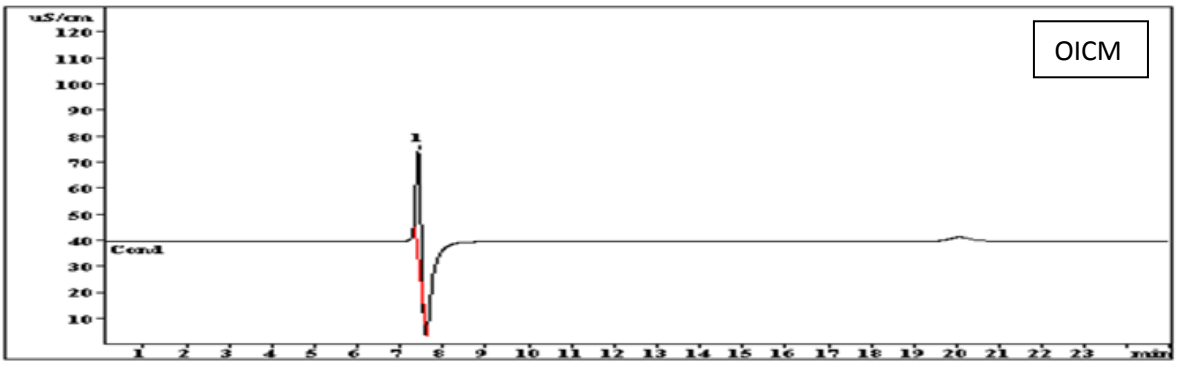


Figure 4.75: Chromatograms of carbon dioxide induced degradation of D14MDEA2MPZ1M identified by OICM.

Table 4.37: Carbon dioxide induced degradation products of D14MDEA2MPZ1M identified by IC methods [Loading (α_L= 0.2, α_R = 0.45), pH (I) = 9.76, pH (F) = 9.47]

Experiment and Analysis		Parameters	
Analytical method: IC	AICM	Peck Level (PL)	1-5
		DGP (PL: 2, 3, 4)	NO_2^-, NO_3^-, PO_4^{3-}
		[DGP], ppm	602.406, 66.636, 955.305
		Std. Verification	RT: 6.09, 8.63, 11.43
	CICM	Peck Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A
	OICM	Peck Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A

4.2.5.2 Degradation Products of D15MDEA2MPZ2M

The chromatogram of AICM for D15MDEA2MPZ2M is shown in figure 4.76. There are five peaks observed in the chromatogram. Peak numbers 2, 3 and 4 are identified which are nitrite, nitrate and phosphate respectively. This sample is analyzed by CICM where as the chromatogram shows two peaks in figure 4.77. In between these two peaks, none of them are identified. Peak number one is probably due to the presence of ammonium radical and other peaks are believed due to the formation of protonated PZ or MDEA. Figure 4.78 shows the chromatogram of OICM for D15MDEA2MPZ2M. Two peaks are found in the chromatogram and both are unknown. It is most probably due to the formation of butyric acid. It could be stated that the identified DGPs of D15MDEA2MPZ2M are nitrate, nitrite and phosphate are summarized in the Table 4.38. Identified DGPs are HSS and the effects are reported in the literature (DOW, 2001; M. S.Islam, 2010; Carlson et al., 2001).

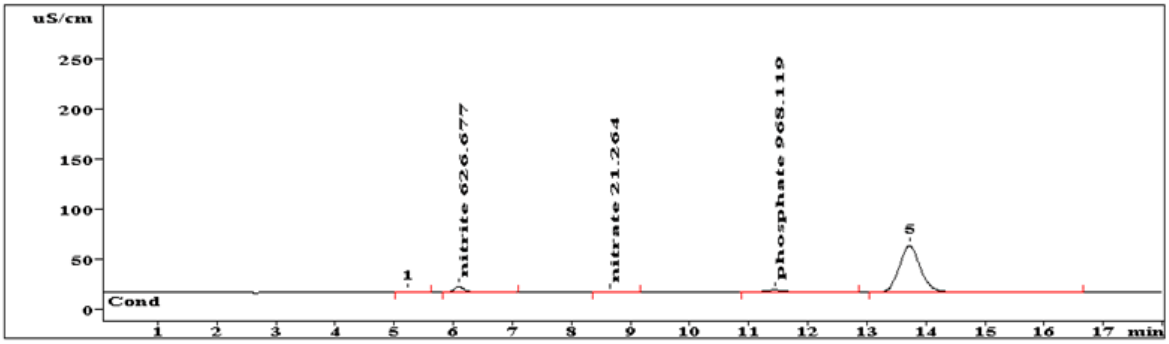


Figure 4.76: Chromatograms of carbon dioxide induced degradation of D15MDEA2MPZ2M identified by AICM.

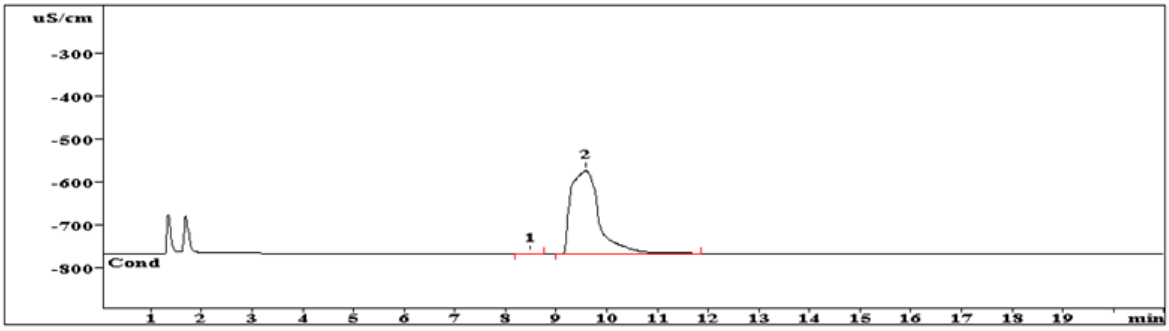


Figure 4.77: Chromatograms of carbon dioxide induced degradation of D15MDEA2MPZ2M identified by CICM.

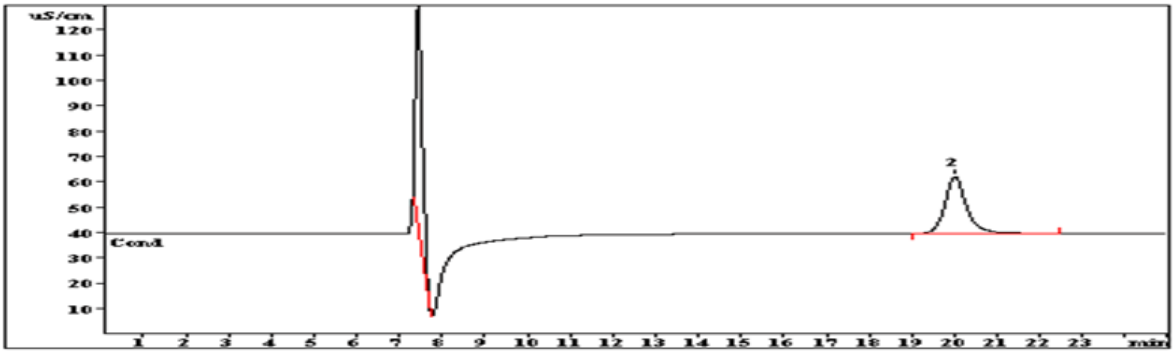


Figure 4.78: Chromatograms of carbon dioxide induced degradation of D15MDEA2MPZ2M identified by OICM.

Table 4.38: Carbon dioxide induced degradation products of D15MDEA2MPZ2M identified by IC methods [Loading (α_L= 0.2, α_R = 0.48), pH (I) = 9.76, pH (F) = 9.47]

Experiment and Analysis		Parameters	
Analytical method: IC	AICM	Peck Level (PL)	1-5
		DGP (PL: 2, 3, 4)	NO_2^-, NO_3^-, PO_4^{3-}
		[DGP], ppm	626.677, 21.246, 968.119
		Std. Verification	RT: 6.09, 8.63, 11.43
	CICM	Peck Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A
	OICM	Peck Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A

4.2.5.3 Degradation Products of D16MDEA3MPZ2M

In order to detect the anionic degradation products of D16MDEA3MPZ2M it is analyzed by AICM and the chromatogram is shown in the figure 4.79. Six peaks are shown in the chromatogram and peak numbers 2, 3 and 4 are identified, these are nitrite, nitrate and phosphate respectively. The chromatogram of CICM is shown in the figure 4.80 for D16MDEA3MPZ2M, three peaks are found in the chromatogram but none of them is identified. It is assumed that peak number one is most probably due to the presence of ammonium. On the other hand rests of the peaks are probably due to the formation of protonated PZ or MDEA. The chromatogram of organic acids ion chromatography (OICM) is shown in the figure 4.81 where as two peaks are observed but none is detected. Finally it was found that identified degradation products of D16MDEA3MPZ2M are nitrite, nitrate and phosphate. The obtained result is supported by the open literature by many researchers (Kadnar, 1999; O. Mrklas, 2003; M. Kaminski, 2002; Closmann et al., 2009).

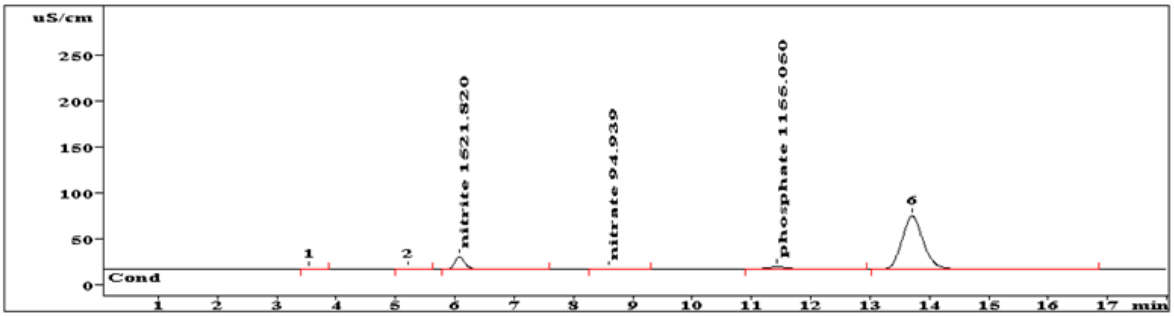


Figure 4.79: Chromatograms of carbon dioxide induced degradation of D16MDEA3MPZ2M identified by AICM.

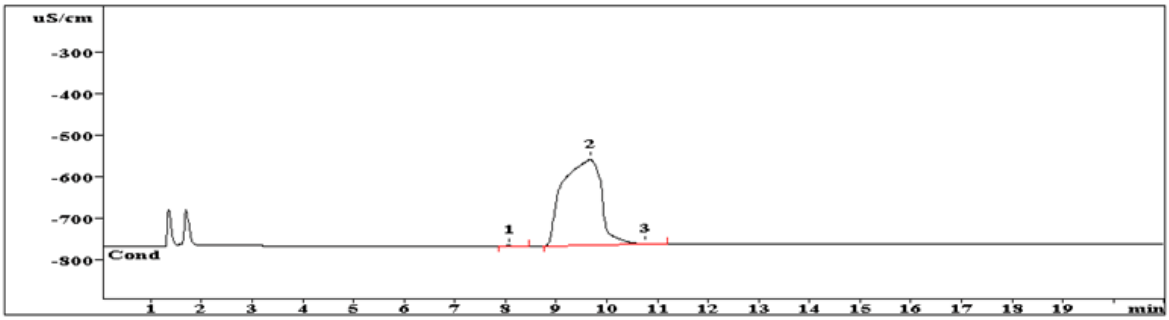


Figure 4.80: Chromatograms of carbon dioxide induced degradation of D16MDEA3MPZ2M identified by CICM.

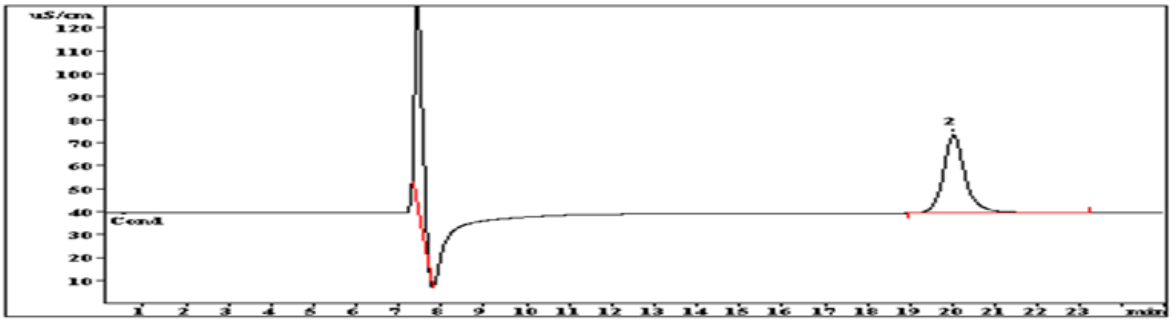


Figure 4.81: Chromatograms of carbon dioxide induced degradation of D16MDEA3MPZ2M identified by OICM.

Table 4.39: Carbon dioxide induced degradation products of D16MDEA3MPZ2M identified by IC methods [Loading (α_L= 0.20, α_R = 0.50), pH (I) = 9.76, pH (F) = 9.47]

Methods			Results
Analytical Method: IC	AICM	Peck Level (PL)	1-6
		DGP (PL: 3, 4, 5)	NO_2^-, NO_3^-, PO_4^{3-}
		[DGP], ppm	1621.82, 94.939, 1166.06
		Std. Verification	RT: 6.07, 8.58, 11.43
	CICM	Peck Level	1, 2, 3
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A
	OICM	Peck Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A

4.2.5.4 Degradation Products of D17MDEA4MPZ2M

The chromatogram of AICM for D17MDEA4MPZ2M is shown in figure 4.82. Two peaks are shown in the chromatogram. Peak number one is identified for nitrite ion of concentration 4.127 and two is not detected. The sample is analyzed twice times using AICM-02 methods and the chromatogram is shown in the figure 4.83. Seven peaks are observed in this chromatogram, peak number five is detected and rests of the peaks are unidentified. However, for this activated sample nitrate is only detected. To detect unknown peaks, this sample is recommended for further analysis by chromatographic methods such as GC/GCMS and HPLC. Figure 4.84 shows the chromatogram of CICM for D17MDEA4MPZ2M, three peaks are shown in the figure but no one is detected. Peak number one is most probably due to the formation of ammonium ion and others are due to the protonated amines or cationic species. The chromatogram of OICM is shown in figure 4.85 where as two peaks are observed and both are undetected. Based on the data analysis it is assumed that peak number two is due to the formation of butyric acid. The identified degradation products are nitrite and nitrate summarized in the Table 4.40.

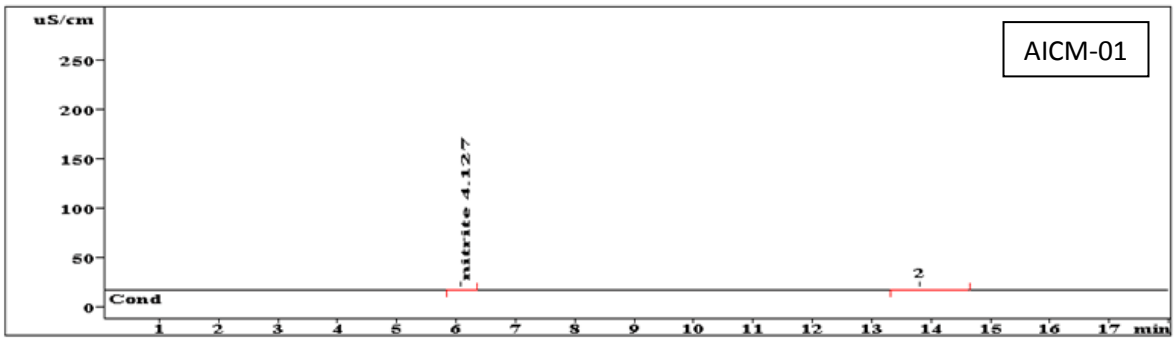


Figure 4.82: Chromatograms of carbon dioxide induced degradation of D17MDEA4MPZ2M identified by AICM-01.

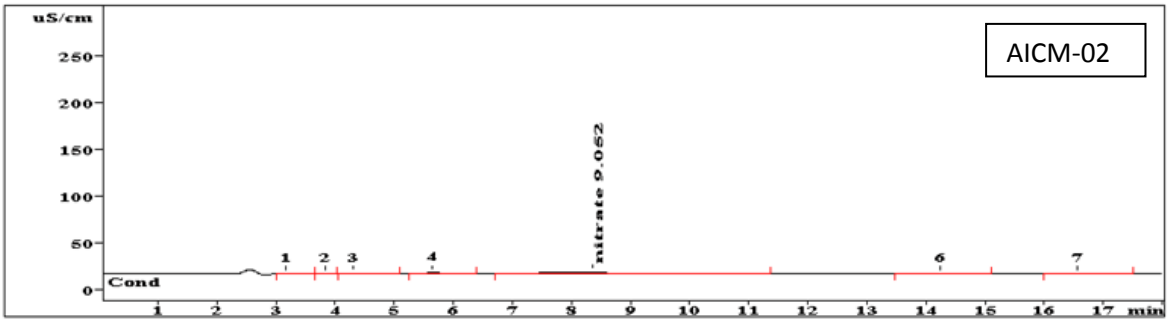


Figure 4.83: Chromatograms of carbon dioxide induced degradation of D17MDEA4MPZ2M identified by AICM-02.

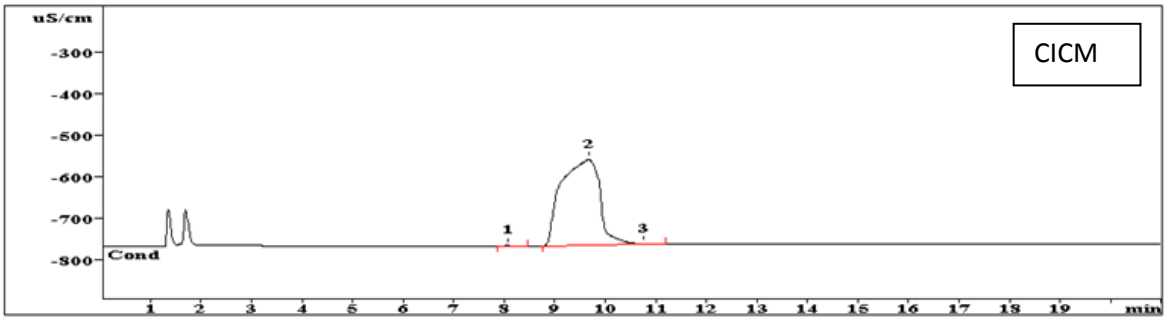


Figure 4.84: Chromatograms of carbon dioxide induced degradation of D17MDEA4MPZ2M identified by CICM.

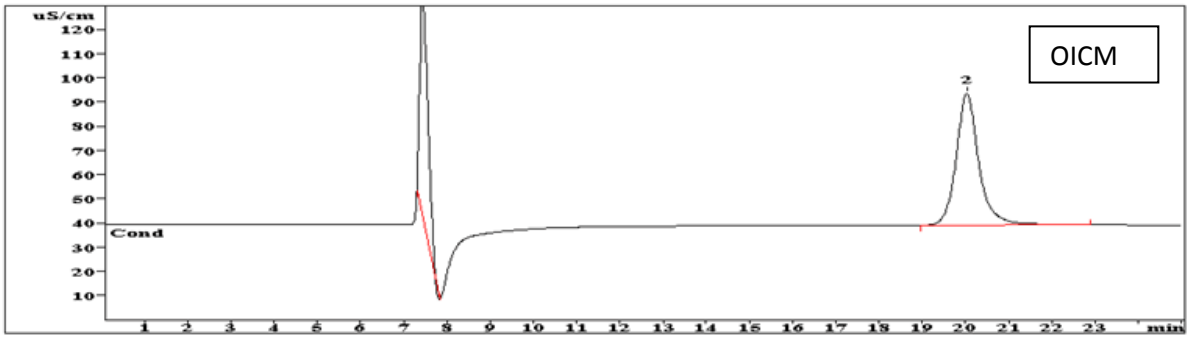


Figure 4.85: Chromatograms of carbon dioxide induced degradation of D17MDEA4MPZ2M identified by OICM.

Table 4.40: Carbon dioxide induced degradation products of D17MDEA4MPZ2M identified by IC methods [Loading (α_L= 0.2, α_R = 0.5), pH (I) = 9.76, pH (F) = 9.47]

Experiment and Analysis		Parameters	
Analytical Method: IC	AICM-01	Peck Level (PL)	1, 2
		DGP (PL: 1)	NO_2^-
		[DGP], ppm	4.127
		Std. Verification	RT: 6.06
	AICM-02	Peck Level (PL)	1-7
		DGP (PL: 5)	NO_3^-
		[DGP], ppm	9.062
		Std. Verification	RT: 8.36
	CICM	Peck Level	1, 2, 3
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A
	OICM	Peck Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A

4.2.5.5 Degradation Products of D18MDEA7MPZ2M

D18MDEA7MPZ2M it is analyzed twice times by AICM and chromatogram is shown in the figure 4.86. Two peaks are shown in the chromatogram and peak number one is identified for nitrite of concentration 3.822. Figure 4.87 shows six peaks for the same sample and acetate is detected as additional anionic DGP for peak number two. In order to identify the cationic DGPs of D18MDEA7MPZ2M it is analyzed by CICM. Figure 4.88 shows the chromatogram of CICM and only one peak is observed but not identified. Since the observed peak showed low area in this case other chromatographic method GC/GCMS and HPLC are recommended to identify such types of unknown peak. The chromatogram of OICM for D18MDEA7MPZ2M is shown in the figure 4.89 where as two peaks are observed but both are unknown. Based on the results it is assumed that peak number two is most probably due to the presence of butyric acid.

Finally it was found that identified degradation products are nitrite and acetate summarized in the Table 4.41. The effects of these DGPs were explained in the open literature and reported by many researchers (DOW, 2001; M. S.Islam, 2010; Carlson et al., 2001).

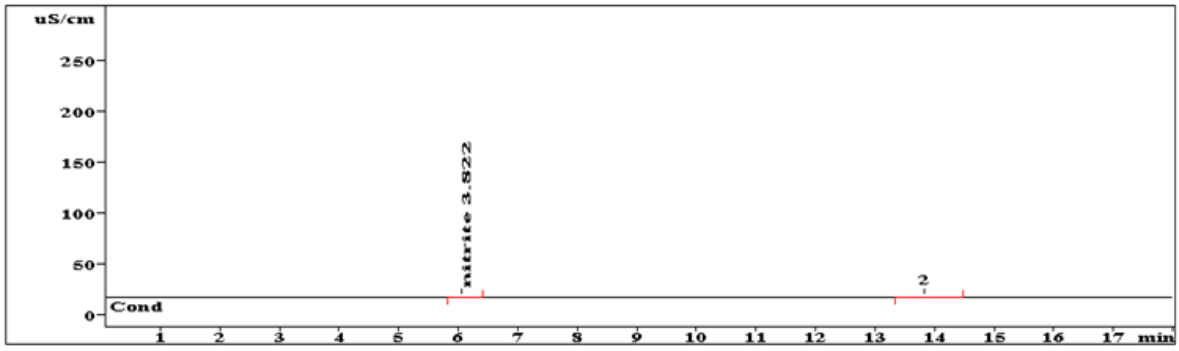


Figure 4.86: Chromatograms of carbon dioxide induced degradation of D18MDEA7MPZ2M identified by AICM-01.

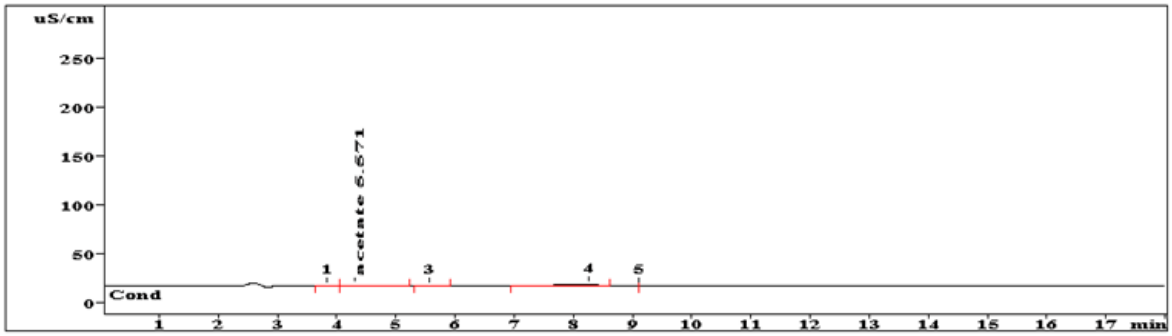


Figure 4.87: Chromatograms of carbon dioxide induced degradation of D18MDEA7MPZ2M identified by AICM-02.

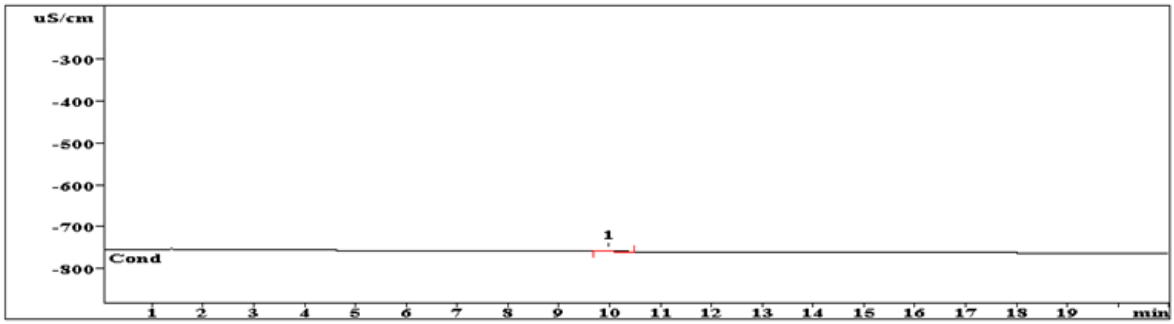


Figure 4.88: Chromatograms of carbon dioxide induced degradation of D18MDEA7MPZ2M identified by CICM.

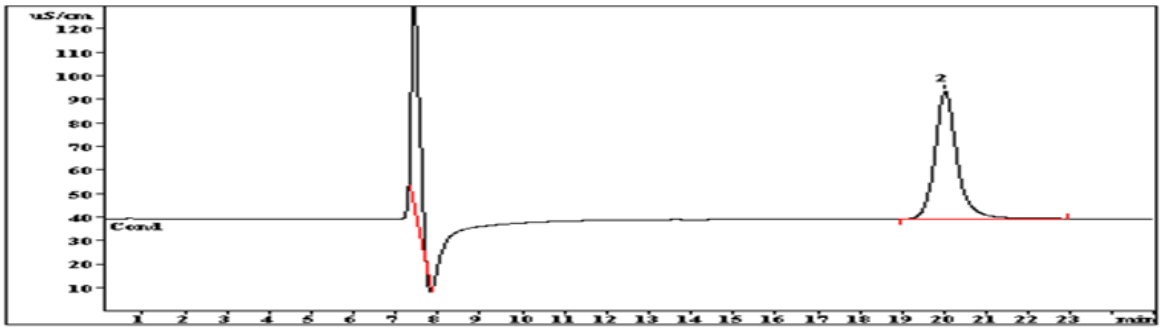


Figure 4.89: Chromatograms of carbon dioxide induced degradation of D18MDEA7MPZ2M identified by OICM

Table 4.41: Carbon dioxide induced degradation products of D18MDEA7MPZ2M identified by IC methods [Loading (α_L= 0.23, α_R = 0.50), pH (I) = 9.76, pH (F) = 9.47]

Experiment and Analysis		**Parameters**	
Analytical Method: IC	**AICM-01**	Peck Level (PL)	1, 2
		DGP (PL: 1)	NO_2^-
		[DGP], ppm	3.822
		Std. Verification	RT: 6.04
	AICM-02	Peck Level (PL)	1-6
		DGP (PL: 2)	Act.
		[DGP], ppm	4.29
		Std. Verification	RT: 5.571
	CICM	Peck Level	1
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A
	OICM	Peck Level	1, 2
		DGP	Unknown
		[DGP], ppm	N/A
		Std. Verification	N/A

4.2.5.6 Variation of Concentration of Ionic DGPs of MDEA+PZ+H_2O+CO_2 System

Figure 4.90 represents the variation of concentration of ionic degradation products for D14MDEA2MPZ1M, D15MDEA2MPZ2M and D16MDEA3MPZ2M. The common DGPs of these samples are nitrite, nitrate and phosphate. The concentration of nitrite and phosphate are found to follow a trend which is increases with amine concentration but nitrate is not. The following table will give us clear concept about the followed trends of DGPs concentration.

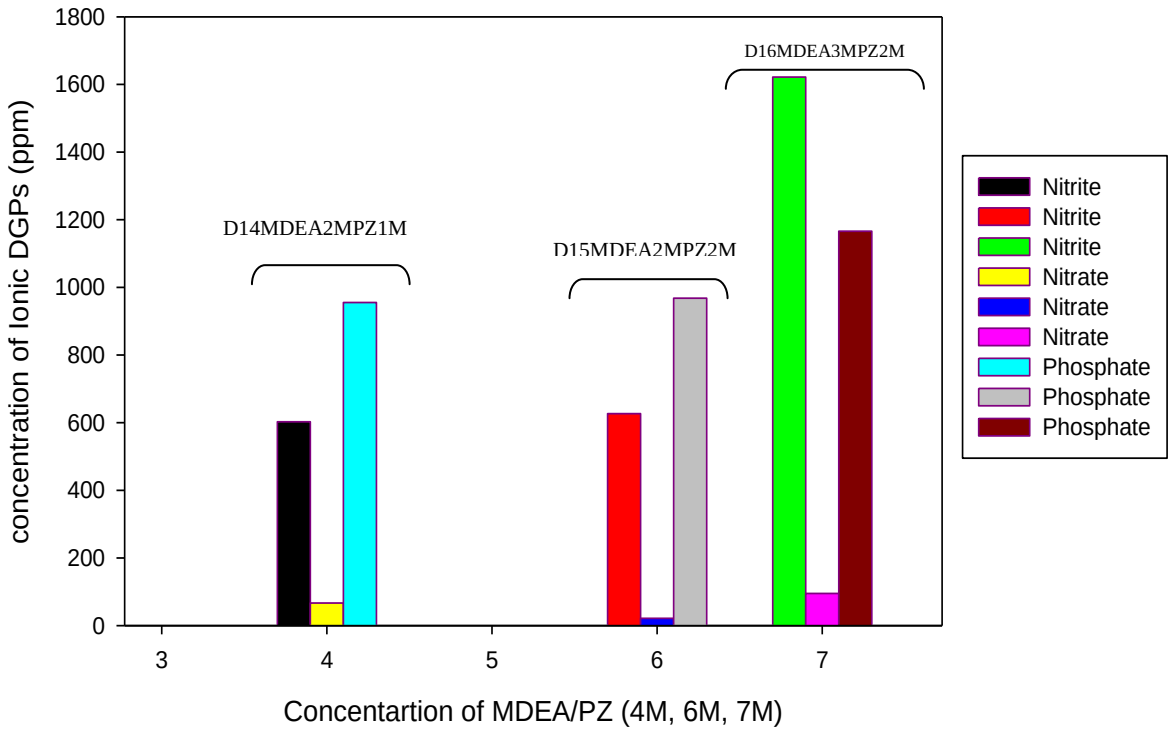


Figure 4.90: Variation of concentration of identified DGPs of D14MDEA2MPZ1M, D15MDEA2MPZ2M and D16MDEA3MPZ2M

The following figure 4.91 represents the variation of ionic DGPs of D17MDEA4MPZ2M and D18MDEA7MPZ2M. The ionic DGPs of D17MDEA4MPZ2M are nitrite and nitrate. On the other hand for D18MDEA7MPZ2M the DGPs are nitrate and acetate. The common degradation products of these two samples are nitrate which is decreases with amine concentration. The other two uncommon degradation products are nitrite and acetate are found with random changed in concentration.

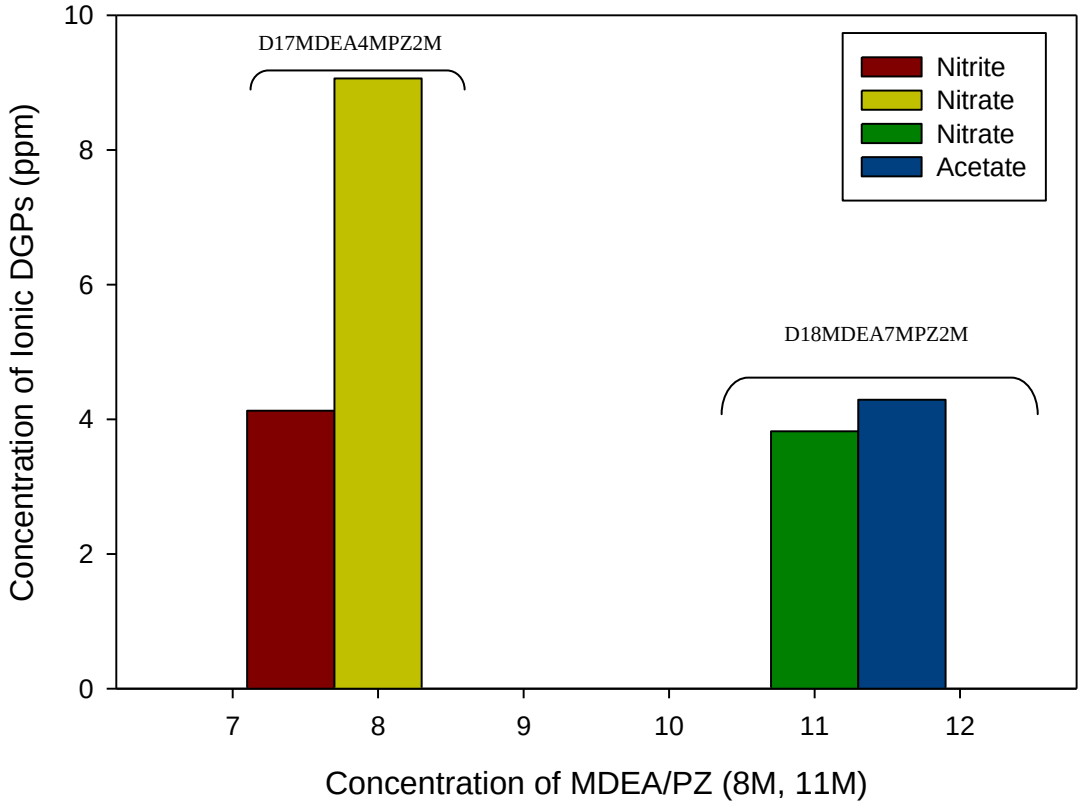


Figure 4.91: Variation of concentration of identified DGPs of D17MDEA4MPZ2M and D18MDEA7MPZ2M

4.2.6 Summary of IC Analysis

In order to identify ionic DGPs, three ion chromatographic analyses were conducted in this degradation study. The IC methods are anionic ion chromatography (AICM), cationic ion chromatography (CICM) and organic acid ion chromatographic method (OICM). Identified degradation products are summarized in the following representation. Ionic DGPs of PZ+H_2O+CO_2 system was given in the table 4.42 for two samples D01PZ1M and D02PZ2M. The most common identified degradation products are acetate, nitrate, phosphate and ammonium. All identified products are the salt of organic and inorganic acids generally referred to as heat stable salt (HSS). The found results are identical with open literature previously many researchers also reported these DGPs during the degradation study of PZ and PZ blends (Stewart and Lanning, 1994; Freeman et al., 2009; Freeman et al., 2010; Alawode, 2005; Sexton and Rochelle, 2010).

Table 4.42: Degradation Products of PZ+H_2O+CO_2 System Identified by IC Method

Sample Code	IC Methods	Formula	M. Weight	Identity	[ppm]
D01PZ1M	AICM, TP: 1-7	CH_3COO^-	59.04	Acetate	1.712
		PO_4^{3-}	94.97	Phosphate	0.199
D02PZ2M	AICM, TP:1-7	NO_3	62.00	Nitrate	6.474
	CICM, TP:1-6	NH_4^+	18.03	Ammonium	0.515

The summarized results DEA+H_2O+CO_2 degradation system for three degraded samples are given in the table 4.43. The identified ionic degradation products are ammonium, acetate, nitrite and phosphate. The most common degradation product is nitrite for all samples. Sample D03DEA2M showed two DGPs and rests of the two samples (D04DEA3M and D05DEA4M) showed four and three degradation products respectively.

Table 4.43: Degradation Products of DEA+H_2O+CO_2 System Identified by IC Method

Sample Code	IC Methods	Formula	Mol. Weight	Identity	[ppm]
D03DEA2M	AICM, TP: 1-5	NO_2^-	46.00	Nitrite	643.19
		PO_4^{3-}	94.97	Phosphate	882.00
D04DEA3M	AICM, TP:1-6	CH_3COO^-	59.04	Acetate	0.814
		NO_2^-	46.00	Nitrite	830.42
		PO_4^{3-}	94.97	Phosphate	956.22
	CICM, TP:1-3	NH_4^+	18.03	Ammonium	0.102
D05DEA4M	AICM, TP:1-8	CH_3COO^-	59.04	Acetate	0.667
		PO_4^{3-}	94.97	Phosphate	2.524
	CICM, TP:1, 2	NH_4^+	18.03	Ammonium	0.500

To the best of our knowledge this degradation studies of DEA+PZ+H_2O+CO_2 System have not yet been studies before. We are first time conducted this experiment. This degradation study is specially undertaken in order to investigate the effect of activator on diethanolamine. Five samples e.g. D06DEA2MPZ1M, D07DEA2MPZ2M, D08DEA3MPZ2M, D09DEA4MPZ2M and D10DEA7MPZ2M of different concentrations were prepared and the summarized results are given in the table 4.44.

In most cases cationic and organic acid ion chromatography no ionic DGP were detected except D10DEA7MPZ2M, this is probably due to the presence of higher concentration of amine and activator. The identified degradation products are nitrite, nitrate, ammonium and phosphate. Based on the number of peaks D06DEA2MPZ1M and D08DEA3MPZ2M these two samples are relatively more stable than rests of the three.

Table 4.44: Degradation Products of DEA+PZ+H_2O+CO_2 System Identified by IC Method

Sample Code	IC Methods	Formula	M. Weight	Identity	[ppm]
D06DEA2MPZ1M	AICM, TP: 1, 2	NO_2^-	46.00	Nitrite	3.369
D07DEA2MPZ2M	AICM, TP: 1-6	NO_2^-	46.00	Nitrite	749.783
		PO_4^{3-}	94.97	Phosphate	958.242
	CICM, TP:1-5	NH_4^+	18.03	Ammonium	0.0000
D08DEA3MPZ2M	AICM, TP:1-6	NO_2^-	46.00	Nitrite	912.967
		PO_4^{3-}	94.97	Phosphate	1033.76
D09DEA4MPZ2M	AICM, TP:1-6	NO_2^-	46.00	Nitrite	2.708
	CICM, TP:1-3	NH_4^+	18.03	Ammonium	0.878
D10DEA7MPZ2M	AICM-01, TP:1-5	NO_2^-	46.00	Nitrite	1604.97
		NO_3	62.00	Nitrate	21.95
		PO_4^{3-}	94.97	Phosphate	1229.81
	AICM-02, TP:1-7	NO_2^-	46.00	Nitrite	1.581
	CICM, TP:1-3	NH_4^+	18.03	Ammonium	6.042

Three degraded samples of MDEA+H_2O+CO_2 system are D11MDEA2M, D12MDEA3M and D13MDEA4M. Table 4.45 focused the summarized ionic DGPs of all samples. The identified degradation products are nitrite, phosphate, acetate and ammonium. The identified common degradation products of these three samples are nitrite and phosphate. MDEA is thermally stable compound it has the greater resistance over primary and secondary amine. In this experiment MDEA was found degradable at lower concentration and highly resistance at higher concentration.

Table 4.45: Degradation Products of MDEA+H_2O+CO_2 System Identified by IC Method

Sample Code	IC Methods	Formula	M. Weight	Identity	[ppm]
D11MDEA2M	AICM-01, TP: 1-6	NO_2^-	46.00	Nitrite	2067.39
		PO_4^{3-}	94.97	Phosphate	18826.0
	AICM-02, TP: 1-7	CH_3COO^-	59.04	Acetate	8.361
		PO_4^{3-}	94.97	Phosphate	0.334
	CICM, TP: 1	NH_4^+	18.03	Ammonium	2.660
D12MDEA3M	AICM-01, TP:1-7	NO_2^-	46.00	Nitrite	329.624
		PO_4^{3-}	94.97	Phosphate	614.307
	AICM-02, TP:1-6	CH_3COO^-	59.04	Acetate	7.046
D13MDEA4M	AICM, TP:1-6	NO_2^-	46.00	Nitrite	1.778
		PO_4^{3-}	94.97	Phosphate	798.231

The identified ionic degradation products of MDEA+PZ+H_2O+CO_2 system for five degraded samples are summarized in table 4.46. Ammonium is not detected sometimes due to the very low concentration. In this work, during analysis many peaks are observed in the chromatogram but few of them are detected. In order to detect unknown peaks further research to be conducted. In organic acid ion chromatographic method no DGP is identified even though sometimes in cationic chromatographic method too. But AICM and CICM can be considered as best and comfort methods for detecting ionic DGPs degraded amine sample.

Table 4.46: Degradation Products of MDEA+PZ+H_2O+CO_2 System Identified by IC Methods

Sample Code	IC Methods	Formula	M. Weight	Identity	[ppm]
D14MDEA2MPZ1M	AICM, TP: 1-5	NO_2^-	46.00	Nitrite	602.406
		NO_3^-	62.00	Nitrate	66.636
		PO_4^{3-}	94.97	Phosphate	955.305
D15MDEA2MPZ2M	AICM, TP: 1-5	NO_2^-	46.00	Nitrite	626.677
		NO_3^-	62.00	Nitrate	21.246
		PO_4^{3-}	94.97	Phosphate	968.119
D16MDEA3MPZ2M	AICM, TP:1-6	NO_2^-	46.00	Nitrite	1621.82
		NO_3^-	62.00	Nitrate	94.939
		PO_4^{3-}	94.97	Phosphate	1166.06
D17MDEA4MPZ2M	AICM-01, TP:1, 2	NO_2^-	46.00	Nitrite	4.127
	AICM-02, TP:1-7	NO_3	62.00	Nitrate	9.062
D18MDEA7MPZ2M	AICM-01, TP:1, 2	NO_2^-	46.00	Nitrite	3.822
	AICM-02, TP:1-6	CH_3COO^-	59.04	Acetate	4.290

4.3 Gas Chromatography Mass Spectroscopy (GC-MS)

Gas Chromatography Mass Spectroscopy (GC-MS) is conducted for D02PZ2M, D05DEA4M, D10DEA7MPZ2M, D13MDEA4M and D18MDEA7MPZ2M of five degradation system. The identified DGPs are discussed in the following section.

4.3.1 Degradation products of D02PZ2M

Figure 4.92 represents the mass spectrum of GC for degraded sample D02PZ2M of degradation system PZ+H_2O+CO_2. The chromatogram shows six identified peaks which are labeled from A to F. The identified degradation products are formamide, ethylenediamine, N-formylpiperazine, formic acid and imidazole. Peak number D is detected for mass spectra of piperazine. The peaks numbers indicated as U are unidentified. The identified DGPs are summarizes in the Table 4.47 and the identification is done on the basis of standard verification method. NIST data base of GC library is also used during identification and the compounds are identified by NIST data base analysis these are formic acid and imidazole. These results are agree with open literatures done by many researchers (Closmann et al., 2009; Freeman et al., 2009; Freeman et al., 2010).

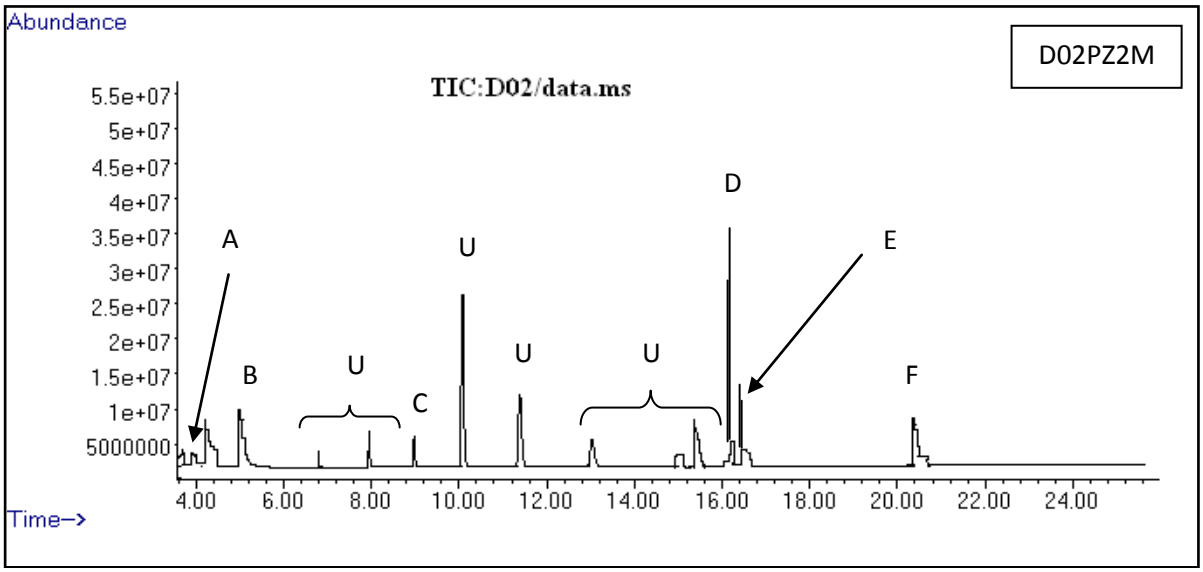


Figure 4.92: Chromatogram of GC mass spectrum of degraded sample D02PZ2M in the degradation system PZ+H_2O+CO_2.

Table 4.47: Degradation Products of D02PZ2M of PZ+H_2O+CO_2 Degradation System Identified by GC-MS and NIST data based Methods.

Sample Code	DGP No.	Peak Level	Peak Area	Observed RT of Peak	Type of Verification	Symbol	M. Formula	M. Weight	Identity
D02PZ2M	1	A	2.374	3.535	Std.V	FM	$HCONH_2$	45.04	Formamide
	2	B	13.290	4.910	Std.V	EDA	$C_2H_4N_2H_4$	60.10	Ethylenediamine
	3	C	4.123	8.752	Std.V	FPZ	$C_5H_{10}N_2O$	114.15	N-formylpiperazine
	4	D	41.199	16.032	Std.V	PZ	$C_4H_{10}N_2$	86.14	Piperazine
	5	E		--	NIST	FA	HCOOH	46.03	Formic Acid
	6	F		--	NIST	--	$C_3H_4N_2$	68.08	Imidazole

4.3.2 Degradation products of D05DEA4M

Figure 4.93 shows the chromatogram of GC-MS spectra of degraded sample D05DEA4M. The indicated peaks of various mass spetra A to I are identified and the unidentified peaks are indicated by U which are not detected by standard verification method. According to the NIST data base analysis the identified DGPs are ethanol and acetone. On the otherhand the identified DGPs are found by standard verification method are formamide, N-(hydroxyethy1) ethylenediamine, oxazolidone, 2-(2-aminoethoxy) ethanol, 2-amino-2-methyl-1-propanol, N,N-bis(hydroxyethy1)- ethylenediamine, ethylurea and 2-methylaminoethanol which are summarized in the Table 4.48. These results are consistent with previous findings by many researchers (Dawodu and A. Meisen, 1996; Dawodu and Meisen, 1991, 1996; Lepaumier et al., 2009c).

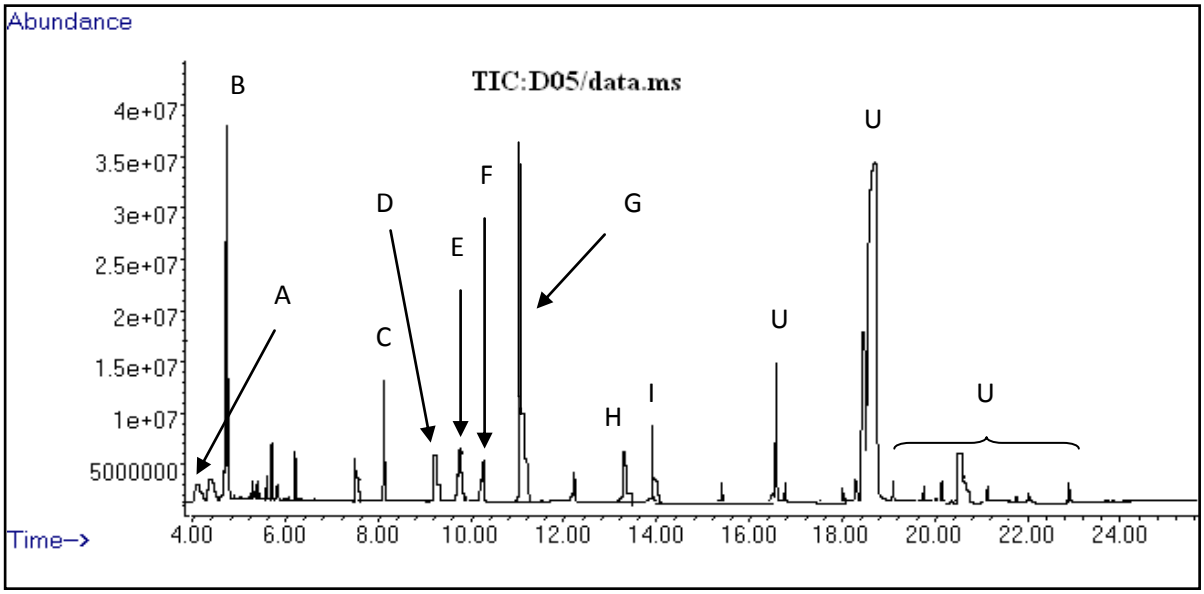


Figure 4.93: Chromatogram of GC mass spectrum of degraded sample D05DEA4M in the degradation system DEA+H_2O+CO_2.

Table 4.48: Degradation Products of D05DEA4M of DEA+H_2O+CO_2 Degradation System Identified by GC-MS Method

Sample Code	DGP No.	Peak Level	Peak Area	Observed RT of Peak	Type of Verification	Symbol	M. Formula	M. Weight	Identity
D05DEA4M	1	A	4.953	3.513	Std.V	FM	$HCONH_2$	45.04	Formamide
	2	B	14.652	5.65	Std.V	HEED	$C_4H_{12}N_2O$	104.15	N-(hydroxyethy1)ethylenediamine
	3	C	7.487	7.9	Std.V	OZD	$C_3H_5NO_2$	87.08	Oxazolidone
	4	D	3.325	9.2	Std.V	DGA	$NH_2CH_2CH_2OCH_2CH_2OH$	105.14	2-(2-aminoethoxy)ethanol
	5	E	3.485	9.8	Std.V	BHEED	$C_6H_{16}N_2O_2$	148.20	N, N-bis(hydroxyethy1)ethylenediamine
	6	F	3.658	10.015	Std.V	AMP	$(CH_3)_2C(NH_2)CH_2OH$	89.14	2-Amino-2-methyl-1-propanol
	7	G	26.874	10.998	Std.V	DEA	$C_4H_{11}NO_2$	105.14	Diethanolamine
	8	H	2.564	13.123	Std.V	EU	$C_3H_9N_2O_2$	105.72	Ethylurea
	9	I	2.987	14.19	Std.V	MAE	$CH_3NHCH_2CH_2OH$	75.11	2-methylaminoethanol
	10	--		--	NIST	--	C_2H_6O	46.07	Ethanol
	11	--		--	NIST	--	C_3H_6O	58.08	Acetone

4.3.3 Degradation products of D10DEA7MPZ2M

The identified mass spectrum of D10DEA7MPZ2M sample is shown in the figure 4.94. The chromatogram of this sample shows significant number of mass spectra indicated by A to I and unknowns are indicated by U, these unknown peaks are identified as acetic acid, glycolic acid, ethylurea and acetone using NIST data base analysis of GCMS. The degradation products identified by standard verification method are formamide, 1,4-Bis(2-hydroxyethyl)piperazine, oxazolidone, 1,4-Dimethylpiperazine, N,N-bis(hydroxyethy1)ethylenediamine, 2-dimethylaminoethanol, 1-(2-Aminoethyl)piperazine and Ethyl-1-piperazinecarboxylate, these are summarized in Table 4.49. The results are consistent with previous findings of many researchers (Dawodu and A. Meisen, 1996; Dawodu and Meisen, 1991, 1996; Lepaumier et al., 2009c).

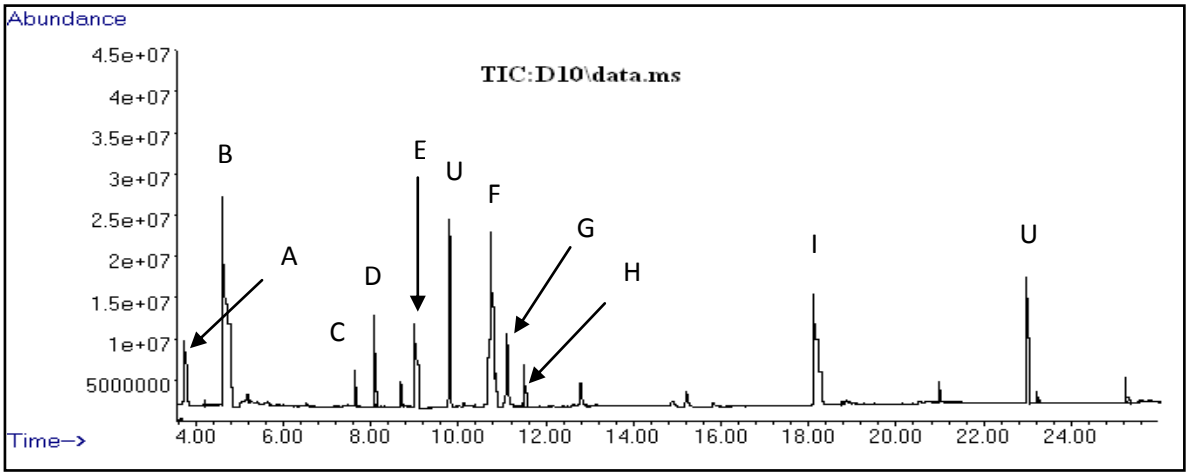


Figure 4.94: Chromatogram of GC mass spectrum of degraded sample D10DEA7MPZ2M in the degradation system DEA+PZ+H_2O+CO_2.

Table 4.49: Degradation Products of D10DEA7MPZ2M of DEA+PZ+H_2O+CO_2 Degradation System Identified by GC-MS Method

Sample Code	DGP No.	Peak Lebel	Peak Area	RT of Peak	Type of Verification	Symbol	M. Formula	M. Weight	Identity
D10DEA7MPZ2M	1	A	5.958	3.350	Std.V	FM	$HCONH_2$	45.04	Formamide
	2	B	21.652	5.145	Std.V	BHEP	$C_8H_{18}N_2O_2$	174.24	1, 4-Bis(2-hydroxyethyl)piperazine
	3	C	2.482	7.842	Std.V	OZD	$C_3H_5NO_2$	87.08	Oxazolidone
	4	D	4.325	8.003	Std.V	DMP	$C_6H_{14}N_2$	114.19	1,4-Dimethylpiperazine
	5	E	4.827	9.650	Std.V	BHEED	$C_6H_{16}N_2O_2$	148.20	N, N-bis(hydroxyethy1)ethylenediamine
	6	F	34.568	10.923	NIST	DEA	$HN(C_2H_4OH)_2$	105.14	Diethanolamine
	7	G	6.421	11.289	Std.V	DMAE	$(CH_3)_2NCH_2CH_2OH$	89.14	2-dimethylaminoethanol
	8	H	1.089	11.592	Std.V	AEP	$C_6H_{15}N_3$	129.20	1-(2-Aminoethyl)piperazine
	9	I	3.985	18.278	Std.V	EPC	$C_7H_{14}N_2O_2$	158.20	Ethyl 1-piperazinecarboxylate
	10	--		--	NIST	--	C_3H_6O	58.08	Acetone
	11	--		--	NIST	EU	$C_3H_8N_2O$	90.64	Ethylurea
	12	--		--	NIST	GA	$HOCH_2COOH$	76.05	Glycolic acid
	13	--		--	NIST	AA	CH_3COOH	60.05	Acetic acid

4.3.4 Degradation products of D13MDEA4M

Figure 4.95 represents the identified peaks of degraded sample D13MDEA4M. This sample consists of 4M methyldiethanolamine. In this figure detected mas spectrum are labeled by letters (A, B, C, D, E, F, G, H, I) and the unknown are indicated by U. The identified DGPs are 1, 4-Bis (2-hydroxyethyl)-piperazine, Bis-(2-hydroxypropyl) amine, Oxazolidone, 2-(2-aminoethoxy)-ethanol, 2-Amino-2-methyl-1-propanol, 2-dimethylaminoethanol, Ethylurea and glycolic acid. From the NIST data base analysis the identified degradation products are acetaldehyde, acetic acid and ethanol. So the total identified DGPs are eleven which are summarized in the Table 4.50. The found degradation products of MDEA induced by CO_2 are previously reported by many researchers which proof the consitancy of this work properly (Lepaumier et al., 2009c, b; Lepaumier et al., 2009a; Lawal et al., 2005b).

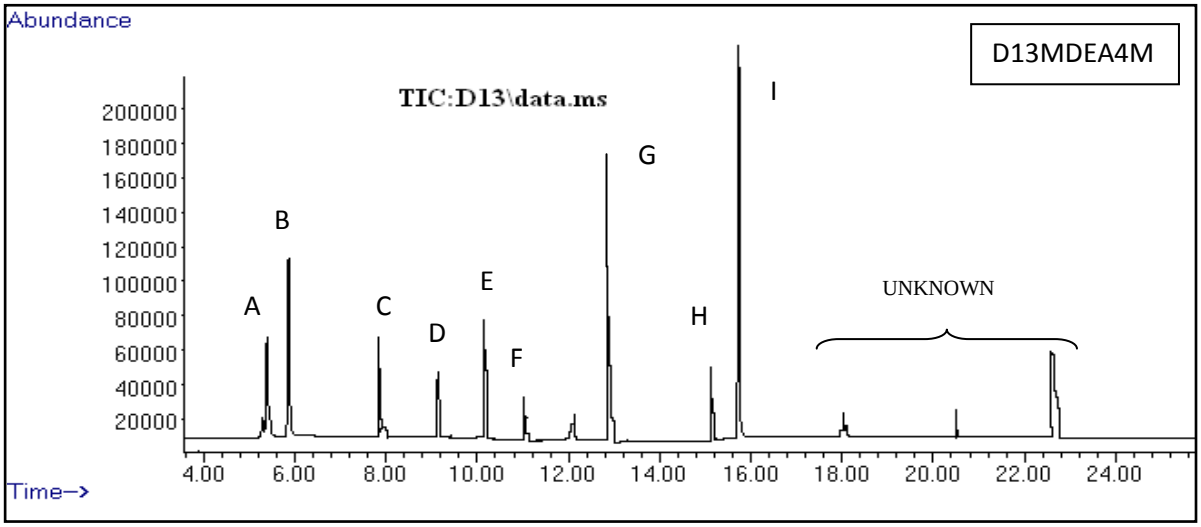


Figure 4.95: Chromatogram of GC mass spectrum of degraded sample D13MDEA4M in the degradation system of MDEA+H_2O+CO_2.

Table 4.50: Degradation Products of D13MDEA4M of MDEA+H_2O+CO_2 Degradation System Identified by GC-MS Method

Sample Code	DGP No.	Peak Lebel	Peak Area (%)	RT of Peak	Type of Verification	Symbol	M. Formula	M. Weight	Identity
D13MDEA4M	1	A	3.354	5.1	Std.V	BHEP	$C_8H_{18}N_2O_2$	174.24	1, 4-Bis(2-hydroxyethyl)piperazine
	2	B	9.556	5.9	Std.V	DIPA	$NH[CH_2CH(OH)CH_3]_2$	133.19	Bis(2-hydroxypropyl) amine
	3	C	3.012	7.9	Std.V	OZD	$C_3H_5NO_2$	87.08	Oxazolidone
	4	D	2.997	9.2	Std.V	DGA	$NH_2CH_2CH_2OCH_2CH_2OH$	105.14	2-(2-aminoethoxy)ethanol
	5	E	4.568	9.9	Std.V	AMP	$(CH_3)_2C(NH_2)CH_2OH$	89.14	2-Amino-2-methyl-1-propanol
	6	F	1.025	11.2	Std.V	DMAE	$(CH_3)_2NCH_2CH_2OH$	89.14	2-dimethylaminoethanol
	7	G	10.698	13.52	Std.V	EU	$C_3H_8N_2O$	90.64	Ethylurea
	8	H	3.894	14.9	Std.V	GA	$HOCH_2COOH$	76.05	Glycolic acid
	9	I	44.265	15.521	Std.V	MDEA	$CH_3N(C_2H_4OH)_2$	119.2	Methyldiethanolamine
	10	--		--	NIST	--	CH_3CHO	44.05	Acetaldehyde
	11	--		--	NIST	--	C_2H_6O	46.07	Ethanol
	12	--		--	NIST	AA	CH_3COOH	60.05	Acetic acid

4.3.5 Degradation products of D18MDEA7MPZ2M

The mass spectrum of D18MDEA7MPZ2M is shown in the figure 4.96. The identified mass spectra are labeled by A, B, C, D, E, F, G, H, I and J and the unknowns are by U. The identified degradation products are 1-Methyl piperazine, 1, 4-Bis(2-hydroxyethyl)piperazine, Bis(2-hydroxypropyl) amine, N, N-dimethyl piperazine, 2-Amino-2-methyl-1-propanol, 2-dimethylaminoethanol, 1-(2-aminoethyl) piperazine and ethanol. The results are in agreement with open literature (Lawal et al., 2005b; Lepaumier et al., 2009c; Closmann et al., 2009). Comparing these results with inactivated MDEA solution it was found that PZ significantly inhibits the degradation process and potentially inceases degradation resistance. The identified DGPs are summarized in the following table 4.51.

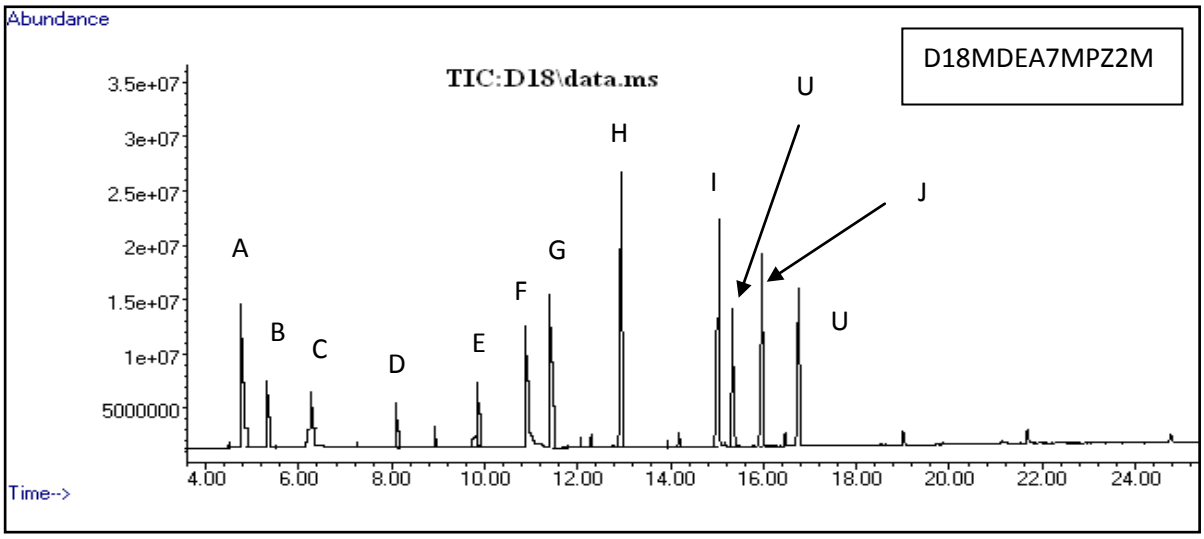


Figure 4.96: Chromatogram of GC mass spectrum of degraded sample D18MDEA7MPZ2M in the degradation system MDEA+PZ+H_2O+CO_2.

Table 4.51: Degradation Products of D18MDEA7MPZ2M of MDEA+PZ+H_2O+CO_2 Degradation System Identified by GC-MS Method

Sample Code	DGP No.	Peak Lebel	Peak Area	Observed RT of Peak	Type of Verification	Symbol	M. Formula	M. Weight	Identity
D18MDEA7MPZ2M	1	A	5.214	4.902	Std.V	MP	$C_5H_{12}N_2$	100.16	1-Methyl piperazine
	2	B	2.894	5.230	Std.V	BHEP	$C_8H_{18}N_2O_2$	174.24	1, 4-Bis(2-hydroxyethyl)piperazine
	3	C	3.612	6.032	Std.V	DIPA	$NH[CH_2CH(OH)CH_3]_2$	133.19	Bis(2-hydroxypropyl) amine
	4	D	3.0254	8.013	Std.V	DMP	$C_6H_{14}N_2$	114.19	N, N- dimethyl piperazine
	5	E	4.365	9.912	Std.V	AMP	$(CH_3)_2C(NH_2)CH_2OH$	89.14	2-Amino-2-methyl-1-propanol
	6	F	4.156	11.201	Std.V	DMAE	$(CH_3)_2NCH_2CH_2OH$	89.14	2-dimethylaminoethanol
	7	G	5.124	11.512	Std.V	AEP	$C_6H_{15}N_3$	129.20	1-(2-aminoethyl) piperazine
	8	H	4.859	--	NIST	--	C_2H_6O	46.07	Ethanol
	9	I	36.231	15.523	Std.V	MDEA	$CH_3N(C_2H_4OH)_2$	119.2	Methyldiethanolamine
	10	J	17.749	16.201	Std.V	PZ	$C_4H_{10}N_2$	86.14	Piperazine

4.3.6 Variation of Peak Areas of DGPs of D02PZ2M, D05DEA4M, D10DEA7MPZ2M, D13MDEA4M and D18MDEA7MPZ2M Identified by GC-MS

Figure 4.97 shows the variation of peak areas for three degradation products of D02PZ2M. The identified degradation products are formamide (FM), ethylenediamine (EDA) and N-formylpiperazine (FPZ). Ethylenediamine occupy highest peak area among all identified DGPs D02PZ2M. Formamide is found very low peak area and N-formyl piperazine is relatively found with greater peak area than FM but lower than EDA. The figure also shows the peak areaof PZ it is almost near about 45% but this is not degradation product. This is a base amine component of D02PZ2M sample.

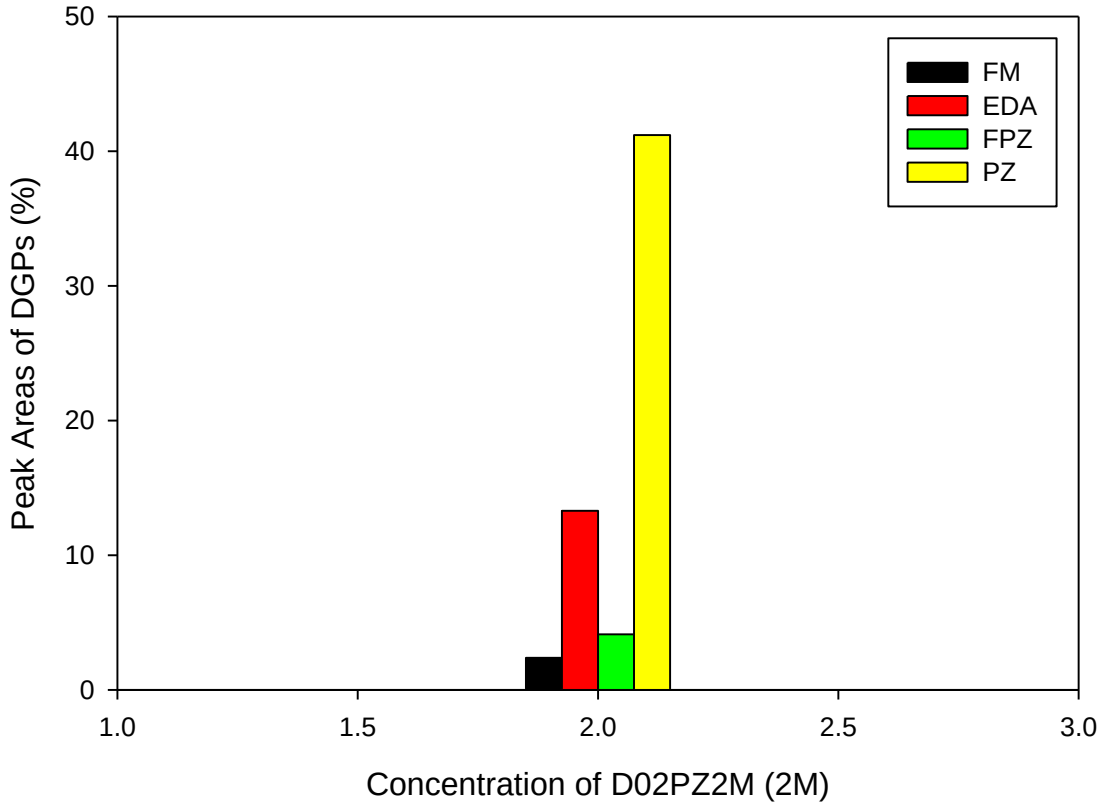


Figure 4.97: Variation of peak areas of DGPs of D02PZ2M identified by GC-MS.

Figure 4.98 (A & B) represents the variation of peak areas of identified degradation products of D05DEA4M and D10DEA7MPZ2M respectively. The common degradation products of these two samples are formamide (FM), oxazolidone (OZD) and bishydroxyethylethylenediamine (BHEED). The peak areas of FM and BHEED are increased with amine concentration but OZD is decreased. The others degradation products of D05DEA4M are HEED, DGA, AMP EU and MAE which peak areas are also shown in the respective figure. The uncommon DGPs of D10DEA7MPZ2M are BHEP, DMP, DMAE, AEP and EPC which are also shown in the figure 4.98B with peak areas.

The variation of peak areas of D13MDEA4M and D18MDEA7MPZ2M are shown in the Figure 4.99A and 4.99B respectively. The common degradation products of these two samples are di-isopropanolamine (DIPA), 2-amino-2-methyl-1-propanol (AMP), Bishydroxyethylpiperazine (BHEP) and 2-dimethylaminoethanol (DMAE). The peak areas of DIPA and BHEP are decreased with amine concentration but DMAE increased. On the other hand AMP shows the same peak areas. The uncommon degradation products of D14MDEA4M are OZD, DGA, EU and GA which also showed in the Figure 4.99A with peak areas. Similarly for D18MDEA7MPZ2M the uncommon DGPs are methyl piperazine (MP), dimethylpiperazine (DMP), aminoethylpiperazine (AEP) and ethanol (EN) are shown in the Figure 4.99B.

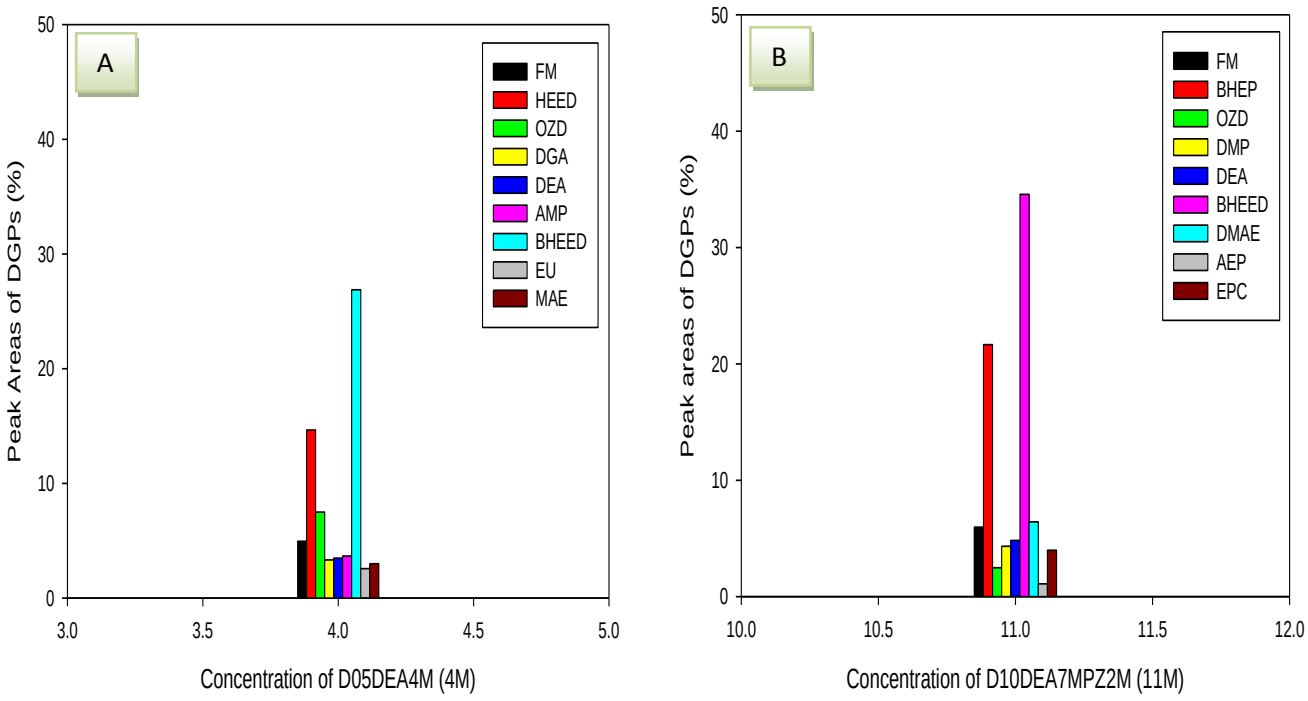


Figure 4.98: Variation of peak areas of DGPs of D05DEA4M and D10DEA7MPZ2M identified by GC-MS.

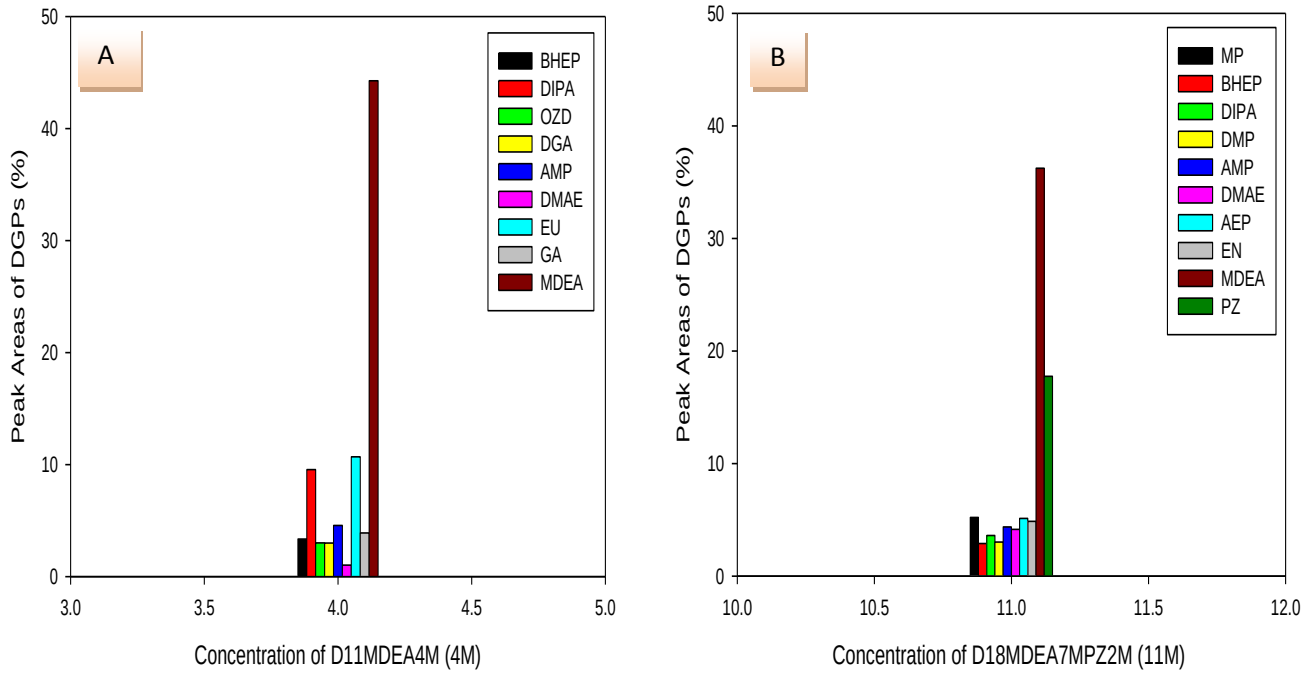


Figure 4.99: Variation of peak areas of DGPs of D11MDEA4M and D18MDEA7MPZ2M identified by GC-MS.

4.3.7 Summary of GC-MS Analysis

The total identified degradation products by GC-MS of five degradation system are summarized in the table 4.52. The detected compounds are shown in the table with verification methods and number of DGPs. In case of D02PZ2M sample three DGPs are identified by standard verification method and two are detected by NIST data base analysis. Ten DGPs are identified for D05DEA4M sample and among these DGPs, eight and two are detected by standard and database analysis trespectively. For tha activated DEA sample D10DEA10MPZ2M, twelve DGPs are identified and in between these twelve eight is found from standard verification methods and four are found from data base analysis. In this work there are eleven DGPs are found from inactivated degraded sample of MDEA (D13MDEA4M) and in between these DGPs, eight and three are detected by standard and NIST data base analysis respectively. Activated MDEA sample (D18MDEA7MPZ2M) shows eight degradation products and one is detected from NIST data base analysis. The rest of the degradation products are obtained fron standard verification. The identity of all degradation products of five degradation system are given in the following table where as the degradation systems are also given accordingly. From this found results it was found that activated samples of amine are comparatively shows lower number of degradation products and inactivated one are shows greater number of DGPs. But among this five degradation sytem only DO2PZ2M this sample shows lowest number of degradation products than other four samples. Activated and inactivated DEA samples shows about same degradation products. The common degradation products of these two sample are Formamide, Oxazolidone, N, N-bis(hydroxyethy1)-ethylenediamine and acetone. However the common DGPs of activated and inactivated MDEA samples are 1, 4-Bis (2-hydroxyethyl)-piperazine, Bis-(2-hydroxypropyl) amine, 2-Amino-2-methyl-1-propanol and 2-dimethylaminoethanol were as the activated one is showed lowest number of degradation products.

Table 4.52: Degradation Products of $PZ+H_2O+CO_2$, $DEA+H_2O+CO_2$, $DEA+PZ+H_2O+CO_2$, $MDEA+H_2O+CO_2$ and $MDEA+PZ+H_2O+CO_2$ Degradation System Identified by GC-MS Method

Sample Code & DS	Type of Verification	Total DGPs	Degradation Products and Identity
D02PZ2M [$PZ+H_2O+CO_2$]	Std.V	3	Formamide, Ethylenediamine, N-formylpiperazine
	NIST	2	Formic Acid, Imidazole
D05DEA4M [$DEA+H_2O+CO_2$]	Std.V	8	Formamide, N-(hydroxyethy1) ethylenediamine, Oxazolidone, 2-(2-aminoethoxy) ethanol, 2-amino-2-methyl-1-propanol, N,N-bis(hydroxyethy1)- ethylenediamine, Ethylurea, 2-methylaminoethanol
	NIST	2	Ethanol, Acetone
D10DEA7MPZ2M [$DEA+PZ+H_2O+CO_2$]	Std.V	8	Formamide, 1,4-Bis(2-hydroxyethyl)piperazine, Oxazolidone, 1,4-Dimethylpiperazine, N,N-bis(hydroxyethy1)ethylenediamine, 2-dimethylaminoethanol, 1-(2-Aminoethyl)piperazine, Ethyl-1-piperazinecarboxylate
	NIST	4	Acetic acid, Glycolic acid, Ethylurea, Acetone
D13MDEA4M [$MDEA+H_2O+CO_2$]	Std.V	8	1, 4-Bis (2-hydroxyethyl)-piperazine, Bis-(2-hydroxypropyl) amine, Oxazolidone, 2-(2-aminoethoxy)ethanol, 2-Amino-2-methyl-1-propanol, 2-dimethylaminoethanol, Ethylurea and glycolic acid.
	NIST	3	Acedaldehyde, Acetic acid, Ethanol
D18MDEA7MPZ2M [$MDEA+PZ+H_2O+CO_2$]	Std.V	7	1-Methyl piperazine, 1, 4-Bis(2-hydroxyethyl)piperazine, Bis(2-hydroxypropyl) amine, N, N- dimethyl piperazine, 2-Amino-2-methyl-1-propanol, 2-dimethylaminoethanol, 1-(2-aminoethyl) piperazine
	NIST	1	Ethanol

[N.B.: Std.V- Standard verification, NIST-National Institute of Standards and Technology, DS-Degradation system]

4.4 Measurement of Viscosity and Density

The physical properties density and viscosity were measured at 30 ˚C, 55 ˚C and 100 ˚C for five degradation system in this experiment. Aqueous amine solutions are prepared at various concentrations of amines and activator (PZ). Inorder to investigate the effect of temperature, concentration and degradation products on the physical properties of alkanolamines are mainly studied here.

4.4.1 Effect of Temperature, Concentration and Degradation Products on Viscosity

4.4.1.1 Effect of Amine Concentration on Viscosity

Figure 4.100 represents the variation of viscosities of activated and inactivated DEA and MDEA alkanolamine with respect to the solution concentrations at constant temperatures 30 ˚C, 55 ˚C and 100 ˚C. Figure 4.100A shows the variation of viscosities for inactivated DEA and MDEA. The inactivated samples of DEA are D03DEA2M, D04DEA3M and D05DEA4M which code numbers are D03, D04 and D05 respectively. Similarly for the inactivated samples of MDEA are D11MDEA2M, D12MDEA3M and D13MDEA4M are shown in the same figure 4.100A with code numbers D11, D12 and D13 respectively. The concentration of these two sets inactivated samples are 2M, 3M and 4M respectively. The found results are indicates that the viscosities are increases with amine concentration which is highest at 4M solution and lowest at 2M. This trend is followed for all inactivated samples of DEA and MDEA. For the inactivated samples of DEA, the viscosities are found to follow this order D03DEA2M< D04DEA3M <D05DEA4M. On the other hand in case of MDEA, the followed order is D11MDEA2M <D12MDEA3M <D13MDEA4M.

Figure 4.100B shows the variation of viscosities for activated DEA and MDEA samples. The activated DEA samples are D06DEA2MPZ1M, D07DEA2MPZ2M, D08DEA3MPZ2M, D09DEA4MPZ2M and D10DEA7MPZ2M which ar shown in the figure 4.100B with code numbers D06, D07, D08, D09 and D10 respectively.

Similarly the code numbers D14, D15, D16, D17 and D18 are shown in the figure 4.100B for D14MDEA2MPZ1M, D15MDEA2MPZ2M, D16MDEA3MPZ2M, D17MDEA4MPZ2M and D18MDEA7MPZ2M. The viscosity of these solutions shows the similar trends like inactivated DEA and MDEA (Fig. 4.100A), it is increased with the alkanolamine concentration. If the amine concentration is increased then viscosities are also increased which showed highest at 11M and lowest at 4M. Finally the variation of viscosities are found to follow this order i.e. D14MDEA2MPZ1M< D15MDEA2MPZ2M< D16MDEA3MPZ2M< D17MDEA4MPZ2M< D18MDEA7MPZ2M. The viscosity of activated DEA samples are found to follow this order i.e. D06DEA2MPZ1M< D07DEA2MPZ2M< D08DEA3MPZ2M< D09DEA4MPZ2M< D10DEA7MPZ2M. This result has better matching with open literature reported by Afshin, Rinker, Derks and Ashour research groups (Derks P. W. J., 2008; Ahmady A., 2011; AI-Ghawas H. A., 1989; Ashour S. S., 1997; Rinker E. B., 1994).

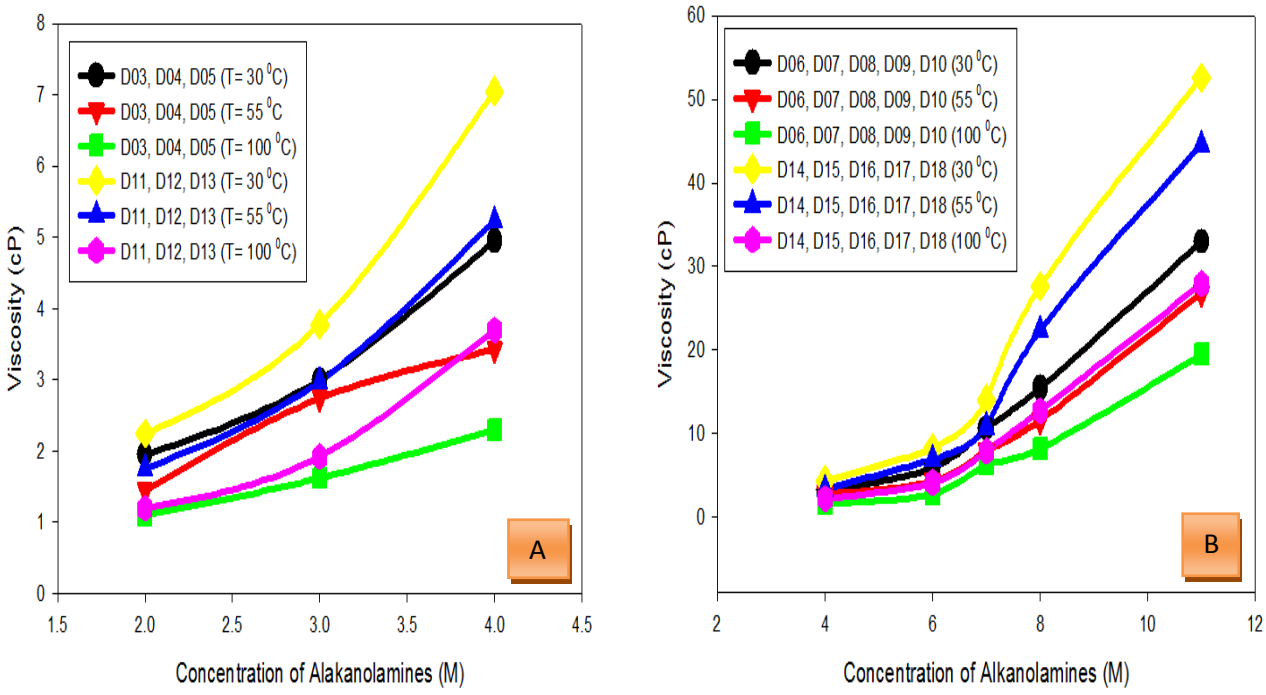


Figure 4.100: Variation of viscosities with alkanolamine concentration for activated and inactivated DEA and MDEA at constant temperture.

4.4.1.2 Effect of Temperature on Viscosity

Figure 4.101 shows the variation of viscosities with temperature for six degraded samples of inactivated DEA and MDEA. The degraded inactivated samples of DEA are D03DEA2M, D04DEA3M and D05DEA4M. The concentrations for thes samples are 2M, 3M and 3M respectively. The results are found to follow this order D03DEA2M< D04DEA3M <D05DEA4M. The highest values of viscosities are found at lowest temperature (25 ˚C) and lowest values viscosities are found at higher temperature (100 ˚C). The degraded inactivated MDEA samples are D11DEA2M, D12DEA3M and D13DEA4M are shown in this figure which concentrations are 2M, 3M and 4M respectively. In case of MDEA, the similar trends are also found for MDEA like DEA and the viscosity of these solutions are found to follow this order D11DEA2M <D12DEA3M <D13DEA4M. To confirm the consistency of this result it was compared with some literature's data and found good correspondence reported by many researchers in case of mixture and individual solutions of alkanolamines (Derks P. W. J., 2008; Ahmady A., 2011; AI-Ghawas H. A., 1989; Ashour S. S., 1997; Rinker E. B., 1994).

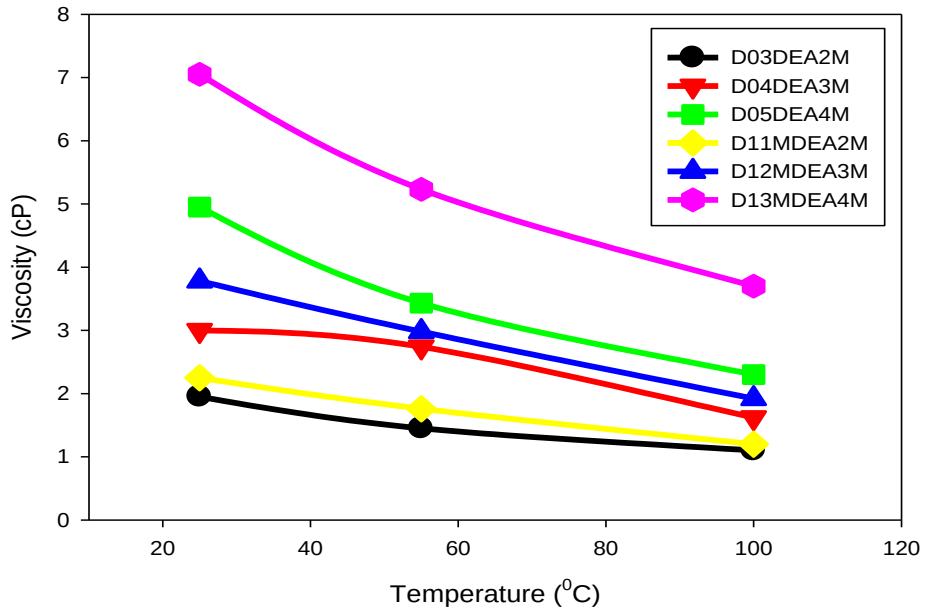


Figure 4.101: Variation of viscosities for inactivated DEA and MDEA at 25 ˚C, 55 ˚C and 100 ˚C temperatures.

Figure 4.102 shows the variation of viscosities for activated DEA and MDEA at 25 ˚C, 55 ˚C and 100 ˚C. The activated DEA samples are D06DEA2MPZ1M, D07DEA2MPZ2M, D08DEA3MPZ2M, D09DEA4MPZ2M and D10DEA7MPZ2M. The viscosities of these solutions are decreased with the increasing of temperature. The viscosity of these five samples are found to follow this order i.e. D06DEA2MPZ1M< D07DEA2MPZ2M< D08DEA3MPZ2M< D09DEA4MPZ2M< D10DEA7MPZ2M.

Figure 4.102 also shows the effect of temperature on the variation of viscosity for five different concentrations of activated MDEA samples such as D14MDEA2MPZ1M, D15MDEA2MPZ2M, D16MDEA3MPZ2M, D17MDEA4MPZ2M and D18MDEA7MPZ2M. The viscosities of these five samples are significantly decreased with the increasing of temperatures. At lower temperature 25 ˚C, the viscosity is found highest and at higher temperature 100 ˚C it is found lowest. Finally the variation of viscosities was found to follow this order D14MDEA2MPZ1M< D15MDEA2MPZ2M< D16MDEA3MPZ2M< D17MDEA4MPZ2M< D18MDEA7MPZ2M. The found results are identical with open literature which reported by many researchers (Derks P. W. J., 2008; Ahmady A., 2011; AI-Ghawas H. A., 1989; Ashour S. S., 1997; Rinker E. B., 1994).

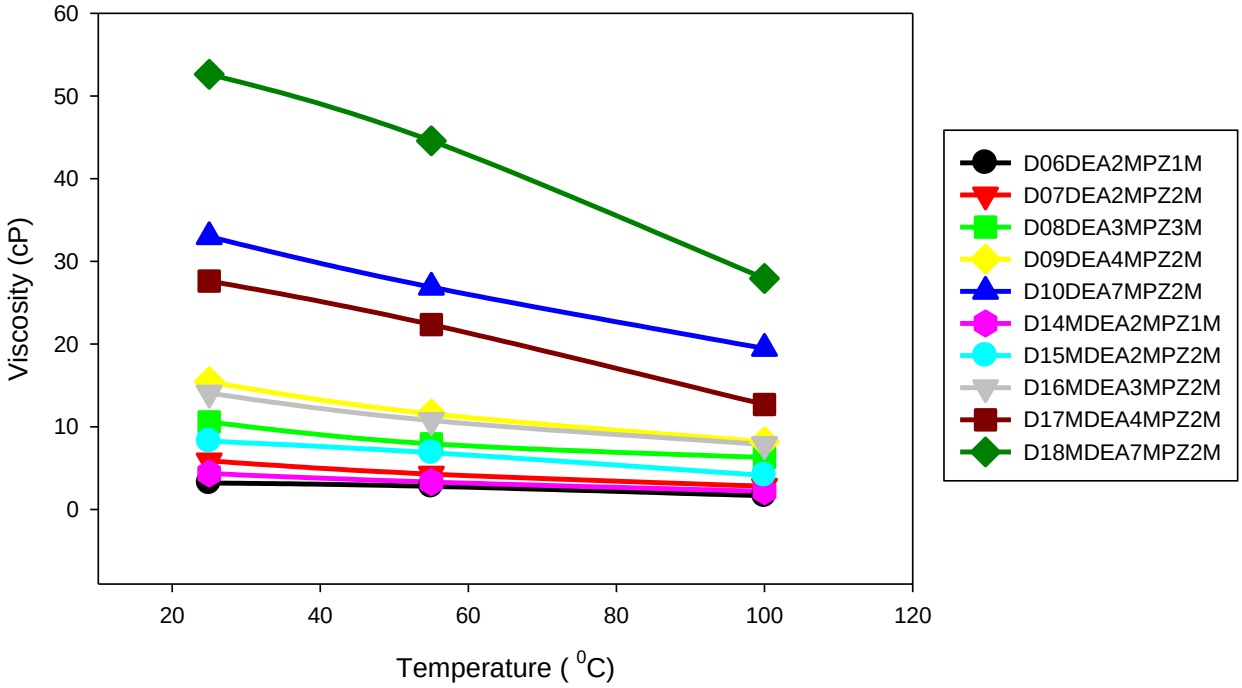


Figure 4.102: Variation of viscosities for activated DEA and MDEA at 25 ˚C, 55 ˚C and 100 ˚C temperatures.

4.4.1.3 Effect of Degradation on Viscosity

Figure 4.103 represents the comparison between the variation of viscosities of virgin and degraded DEA and MDEA solutions at the temperature 30 ˚C. The degraded and virgin solutions are indicated by DS and VS respectively. Figure 4.103A shows the comparison of viscosities for inactivated DEA and MDEA. The inactivated samples of DEA are D03DEA2M, D04DEA3M and D05DEA4M which code numbers are D03, D04 and D05 respectively. On the other hand the inactivated samples of MDEA are D11MDEA2M, D12MDEA3M and D13MDEA4M are shown with code numbers D11, D12 and D13 respectively. The concentrations of these two sets samples are 2M, 3M and 4M respectively. The found results indicate that the viscosities of virgin amine solutions are lower than degraded one and it is increaseed with amine concentration.

Figure 4.103B shows the comparison of viscosities for activated DEA and MDEA samples. The activated DEA samples are D06DEA2MPZ1M, D07DEA2MPZ2M, D08DEA3MPZ2M, D09DEA4MPZ2M and D10DEA7MPZ2M which shown in the figure with code numbers D06, D07, D08, D09 and D10 respectively. Similarly the code numbers D14, D15, D16, D17 and D18 are shown for D14MDEA2MPZ1M, D15MDEA2MPZ2M, D16MDEA3MPZ2M, D17MDEA4MPZ2M and D18MDEA7MPZ2M respectively. The final results are found to follow the similar trends like inactivated one. The viscosities of degraded solutions are found greater than virgin solutions. From this results it could be stated that, degradation of amine makes the solution more viscuss and it is significantly reduced the solution flow rate through the pipe lines.

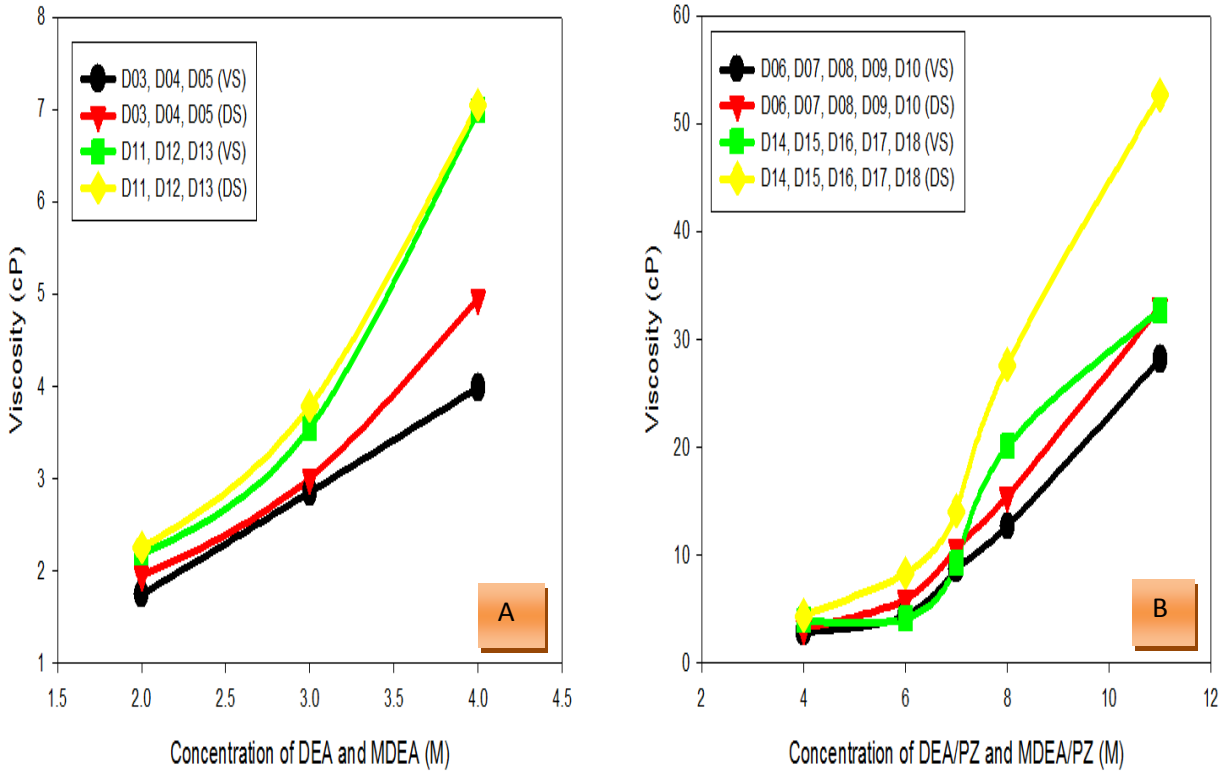


Figure 4.103: Comparison between the viscosities of virgin and degraded amine solutions for activated and inactivated DEA and MDEA at 25 ˚C temperature.

4.4.2 Effect of Temperature, Concentration and Degradation Products on Density

4.4.2.1 Effect of Concentration on Density

Figure 4.104 represents the variation of densisties with concentration for activated and inactivated DEA and MDEA samples. The all samples are shown in the figure with specific code numbers. The inactivated samples of DEA are D03DEA2M, D04DEA3M and D05DEA4M shown by the code numbers D03-D05 in the figure 4.104A at 30 ˚C, 55 ˚C and 100 ˚C. In case of MDEA, the samples D11MDEA2M, D12MDEA3M and D13MDEA4M are also shown in the same figure by the code numbers D11-D13 at the same temperatures. The concentration of these two sets samples are 2M, 3M and 4M respectively. From this result it was found that the densities are increased with amine concentration. The highest values of densities are found at 4M concentration and lowest values are at 2M concentration.

In case of activated DEA and MDEA samples the results are found to follow the similar trends which given in the figure 4.104B. The highest values of densities are found at 11.0 (M) concentration and lowest are at 4.0 (M). The activated samples of DEA are D06DEA2MPZ1M, D07DEA2MPZ2M, D08DEA3MPZ2M, D09DEA4MPZ2M, and D10DEA7MPZ2M which code numbers are D06 to D10 shown in the figure 4.104B at the same temperatures. On the other hand D14, D15, D16, D17 and D18 code numbers are shown for D14MDEA2MPZ1M, D15MDEA2MPZ2M, D16MDEA3MPZ2M, D17MDEA4MPZ2M and D18MDEA7MPZ2M respectively.

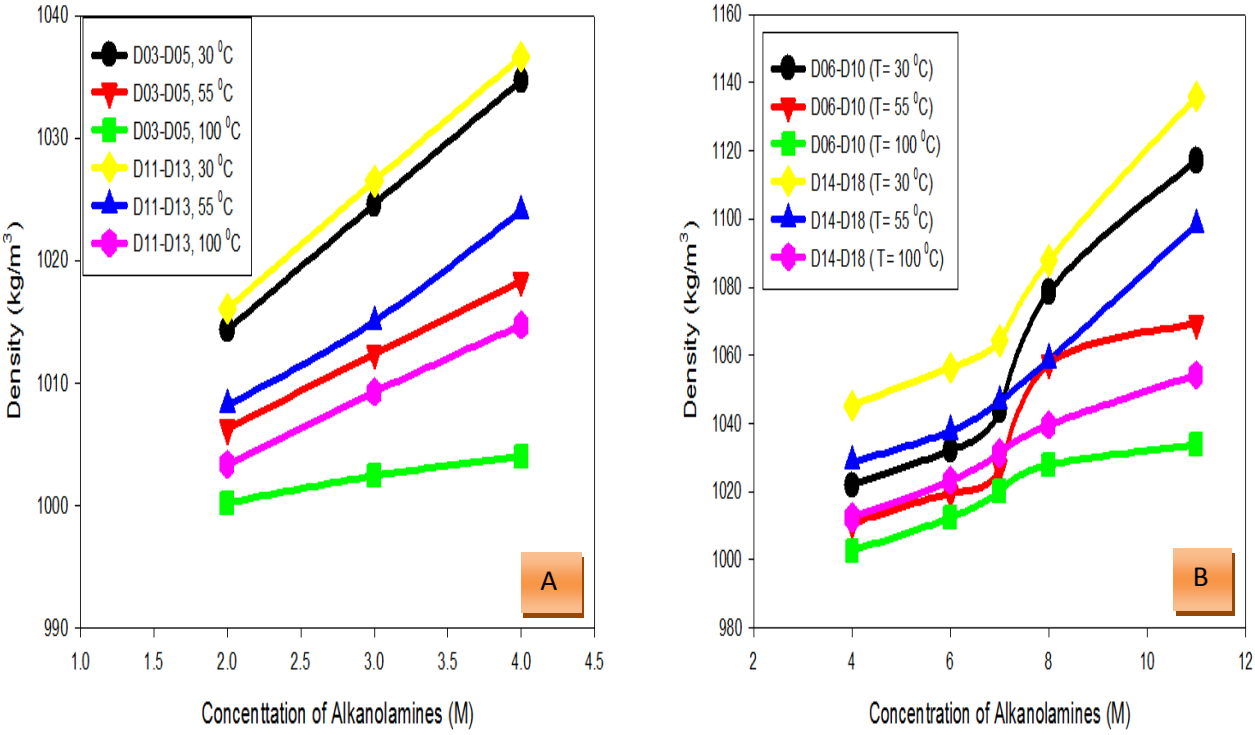


Figure 4.104: Variation of densities with alkanolamine concentration for activated and inactivated DEA and MDEA at 30 ˚C, 55 ˚C and 100 ˚C tempertures.

4.4.2.2 Effect of Temperature on Density

The variation of densities with temperature for inactivated DEA and MDEA are shown in the Figure 4.105 at 25 ˚C, 55 ˚C and 100 ˚C temperatures. The inactivated samples of DEA are D03DEA2M, D04DEA3M and D05DEA4M. On the other hand the inactivated samples of MDEA are D11MDEA2M, D12MDEA3M and D13MDEA4M. In both cases the densities are decreases with increasing of temperatures and the highest value of densities are found at 25 ˚C temperature. At 100 ˚C temperature the densities are found lowest. The found results are identical with open literature which reported by many researchers (Derks P. W. J., 2008; Ahmady A., 2011; AI-Ghawas H. A., 1989; Ashour S. S., 1997; Rinker E. B., 1994).

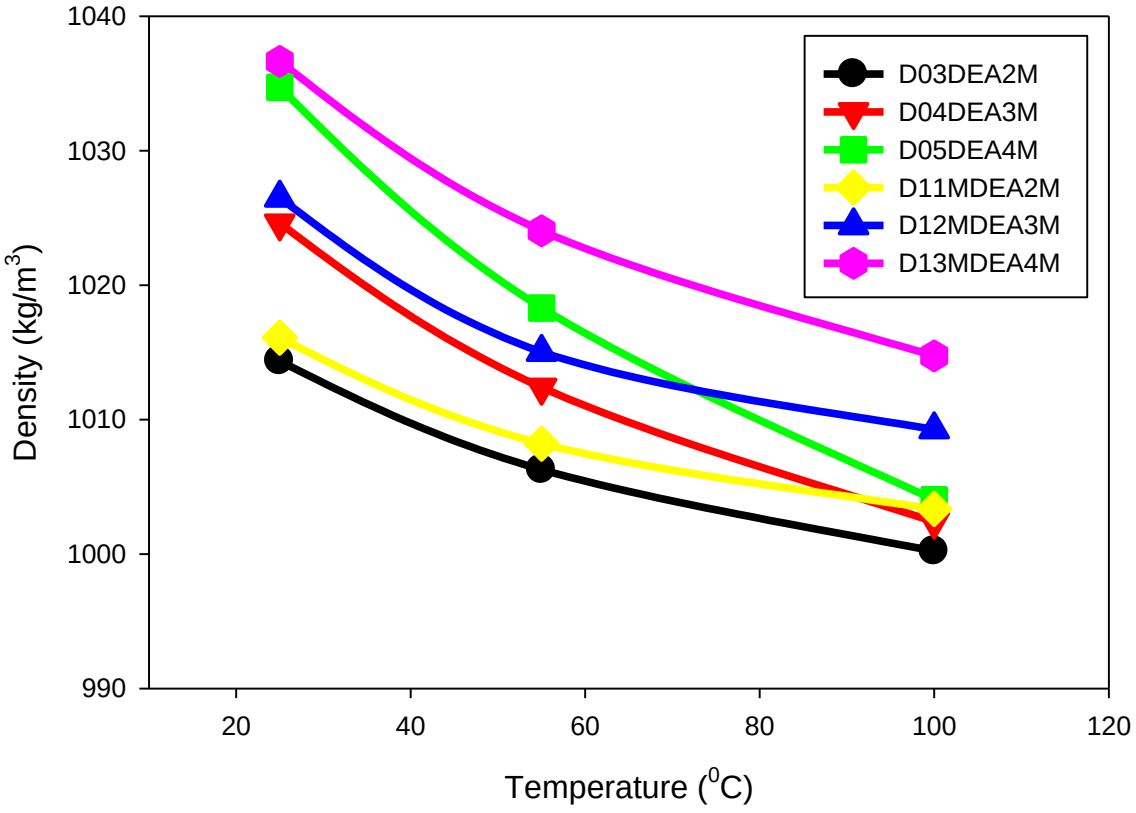


Figure 4.105: Variation of densities for inactivated DEA and MDEA at 25 ˚C, 55 ˚C and 100 ˚C temperatures.

Figure 4.106 represents the variation of densities with temperature for activated DEA and MDEA. The activated samples of DEA are D06DEA2MPZ1M, D07DEA2MPZ2M, D08DEA3MPZ2M, D09DEA4MPZ2M, and D10DEA7MPZ2M. On the other hand, activated samples of MDEA are D14MDEA2MPZ1M, D15MDEA2MPZ2M, D16MDEA3MPZ2M, D17MDEA4MPZ2M and D18MDEA7MPZ2M respectively, shown in the same figure. The variations of densities of these samples are decreasing with increasing of temperature. The highest and lowest values of densities are observed at 25 ˚C and 100 ˚C temperatures.

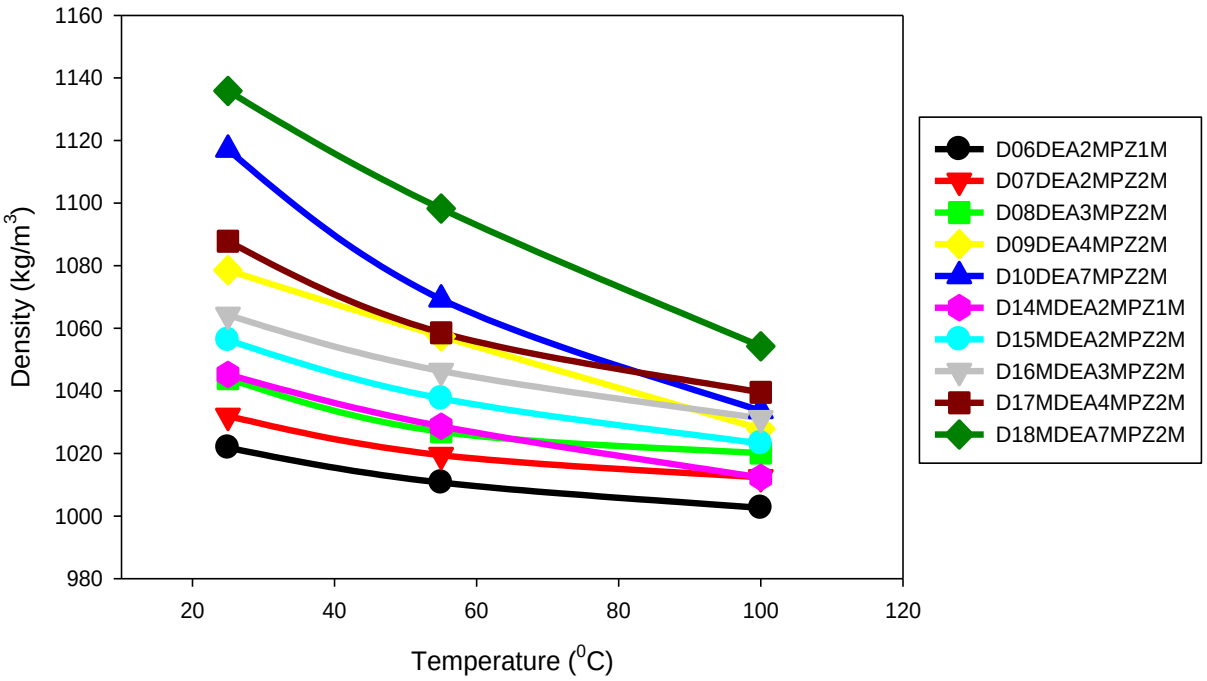


Figure 4.106: Variation of densities for activated DEA and MDEA at 25 ˚C, 55 ˚C and 100 ˚C temperatures.

4.4.2.3 Effect of Degradation on Density

A comparative study of densities of virgin and degraded solution for activated and inactivated DEA and MDEA at 30 ˚C temperature are shown in the Figure 4.107. The degraded and virgin solutions are indicated by DS and VS respectively. Figure 4.107A shows the comparison of densities for inactivated DEA and MDEA. The inactivated samples of DEA are D03DEA2M, D04DEA3M and D05DEA4M which shown in the figure by code numbers D03, D04 and D05 respectively. In case of MDEA, the samples D11MDEA2M, D12MDEA3M and D13MDEA4M are shown by D11, D12 and D13 respectively. The concentrations of these two sets samples are 2M, 3M and 4M respectively.

The activated DEA samples are D06DEA2MPZ1M, D07DEA2MPZ2M, D08DEA3MPZ2M, D09DEA4MPZ2M and D10DEA7MPZ2M which shown in the figure by the code numbers D06, D07, D08, D09 and D10 respectively. Similarly the code numbers D14, D15, D16, D17 and D18 are used for activated MDEA samples D14MDEA2MPZ1M, D15MDEA2MPZ2M, D16MDEA3MPZ2M, D17MDEA4MPZ2M and D18MDEA7MPZ2M respectively. The concentration of these two sets samples are 4M, 6M, 7M, 8M and 11M. In both cases, the found results are indicates that, the viscosities of virgin amine solutions are lower than the degraded one and it is increaseed with amine concentration. The degradation of alkanolamines significantly reduced the aqueous part of the solution by vaporization at stripper conditions and the addition of various agents also affects the densities as a result DS shows high values.

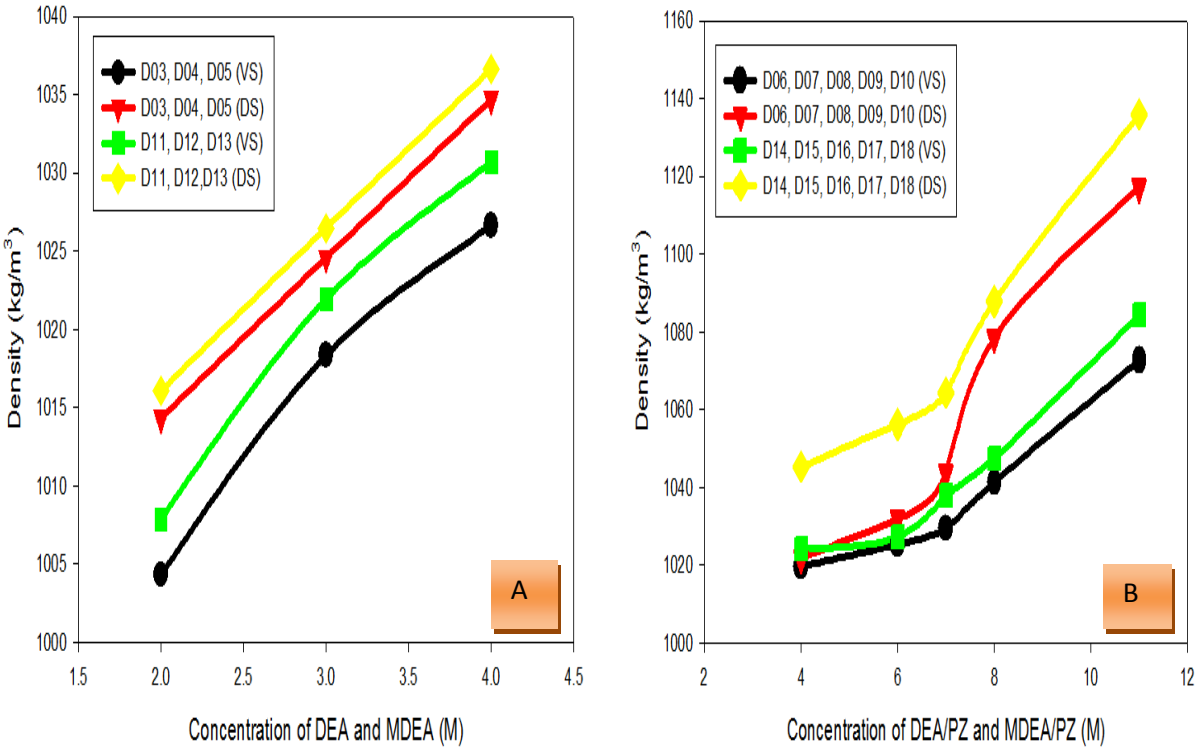


Figure 4.107: Comparison between the densities of virgin and degraded amine solutions for activated and inactivated DEA and MDEA at 30 ˚C temperature.

4.4.3 Role of Degradation Products on Density and Viscosity

The degradation products play an important role on the physical properties of alkanolamines. In this present studies the degradation produvts are identified by various chromatographic methods which are mostly ionic and molecular spcies. The concentrations of all degradation products are determined and their effects are discussed as well individually in the following section. In the HPLC analysis the FM, AEE, MOE and EN are identified and their variation of peak areas are shown in the Figure 4.108. In this figure MOE is only decreased at 4M concentration, otherwise the peak areas for rest of the ions are shown increased. Since the peak areas are increased with amine concentration so it will increase the density and viscosity of the amine solutions.

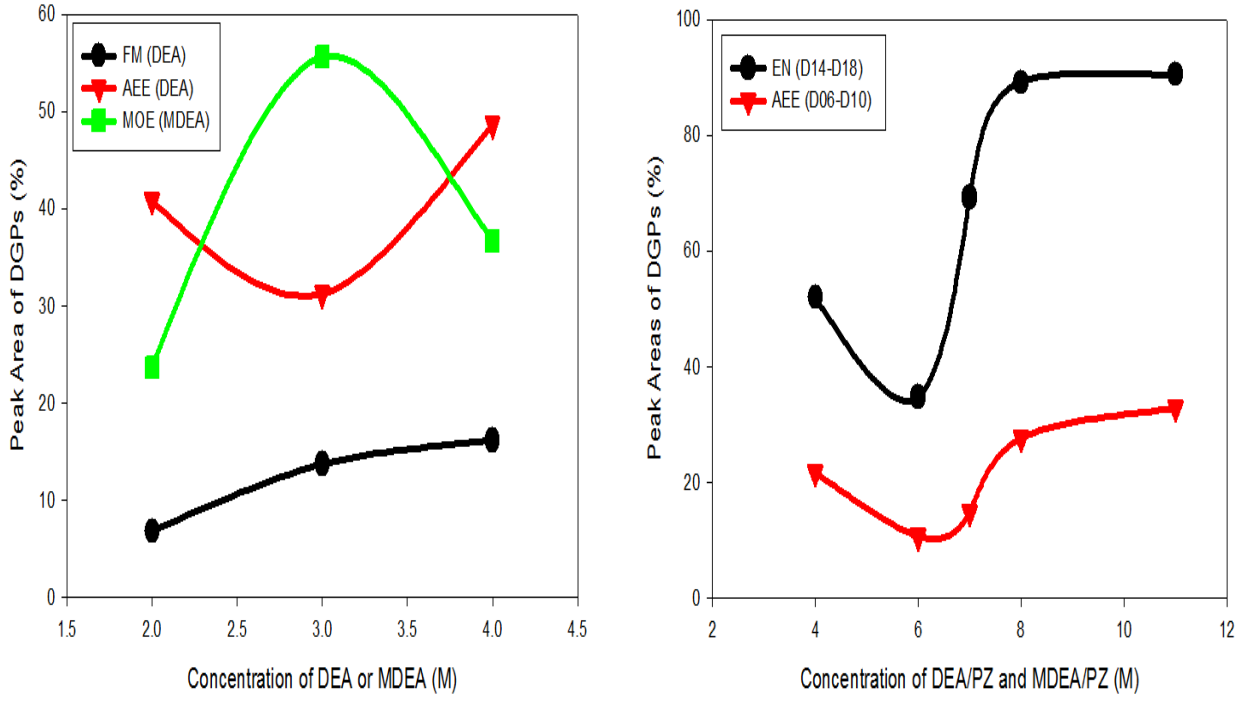


Figure 4.108: Variation of peak ares of identified degradation products of activated and inactivated DEA and MDEA by HPLC.

Figure 4.109 shows the peak ares of identified DGPs of activated DEA and MDEA. The identified DGPs are molecular species which are FM, MOE and EPC. These degradation products are finally decreased with amine concentration so it will decrease the physical properties of alkanolamines. In the above section we have already discussed that the concentration significantly increased the density and viscosity of the solution. Since the concentrations of DGPs are decreases so it will obviously dcrease the value of density and viscosity.

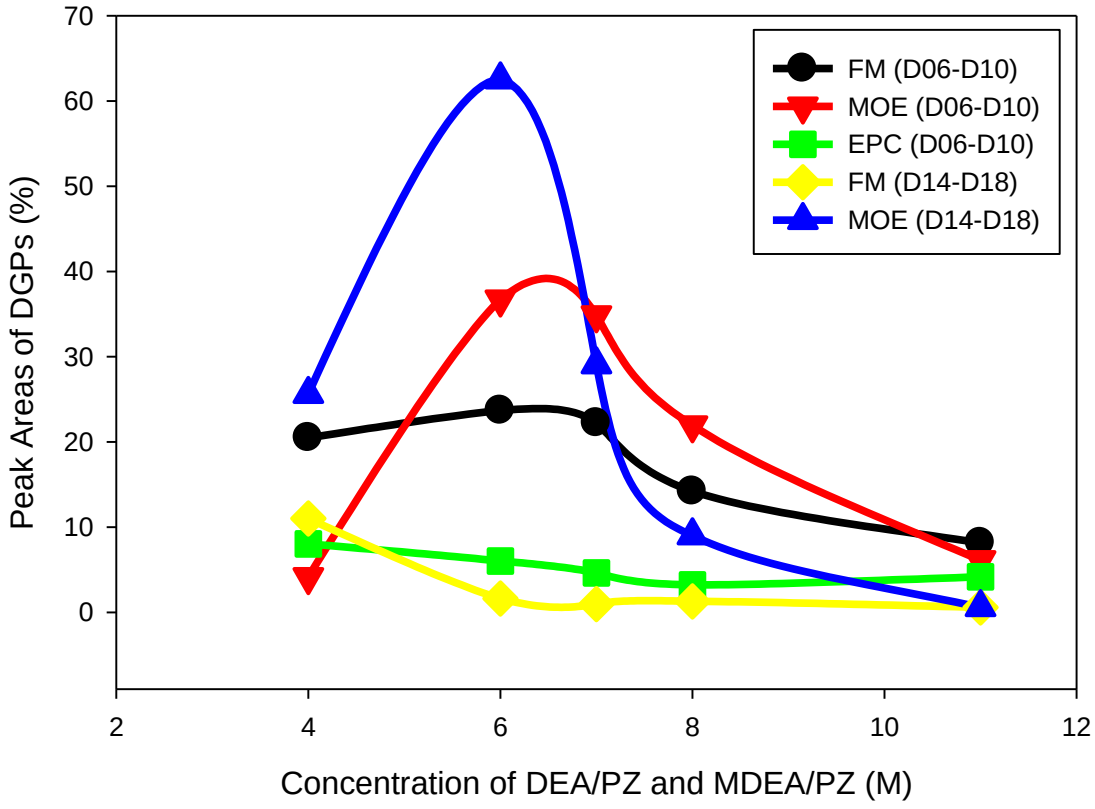


Figure 4.109: Variation of peak ares of identified degradation products of DEA/PZ and MDEA/PZ by HPLC.

In the gas chromatography mass spectroscopy (GC-MS) analysis, the molecular DGPs such as DMAE, AMP, BHEP, OZD and FM are also detected for activated and inactivated DEA and MDEA. The concentration of AMP, FM and DMAE are increased with alkanolamine concentration. Since their concentrations are increased so it will increases the physical properties of amine solutions. On the other hand the peak ares of BHEP and OZD are decreases with amine concentration so it will decreases the density and viscosity of alkanolamines.

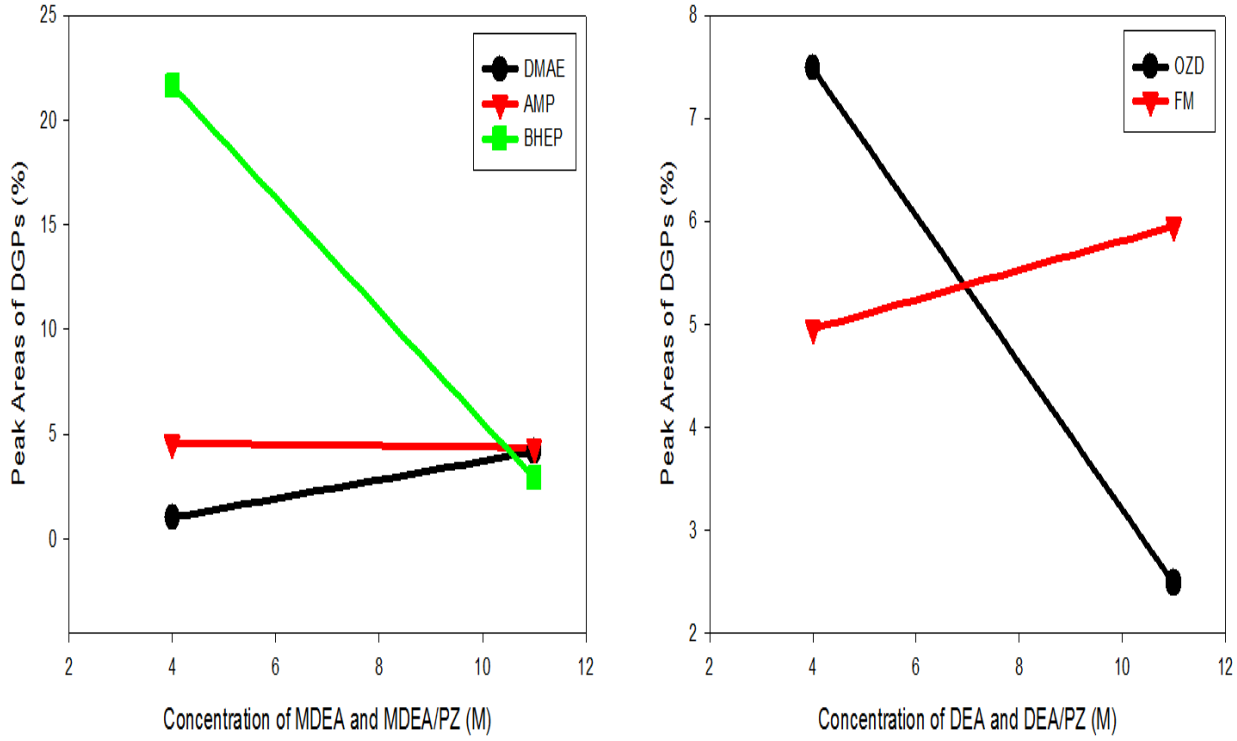


Figure 4.110: Variation of peak ares of identified degradation products of activated and inactivated DEA and MDEA by GCMS.

In the ion chromatographic (IC) analysis, nitrite and phosphate are identified for DEA/PZ and MDEA/PZ samples. The concentration of these two ions are increased with amine concentrtions. Since the concentration of these both ions are increased so it will increase the dnsity and viscosity of the alkanolamines.

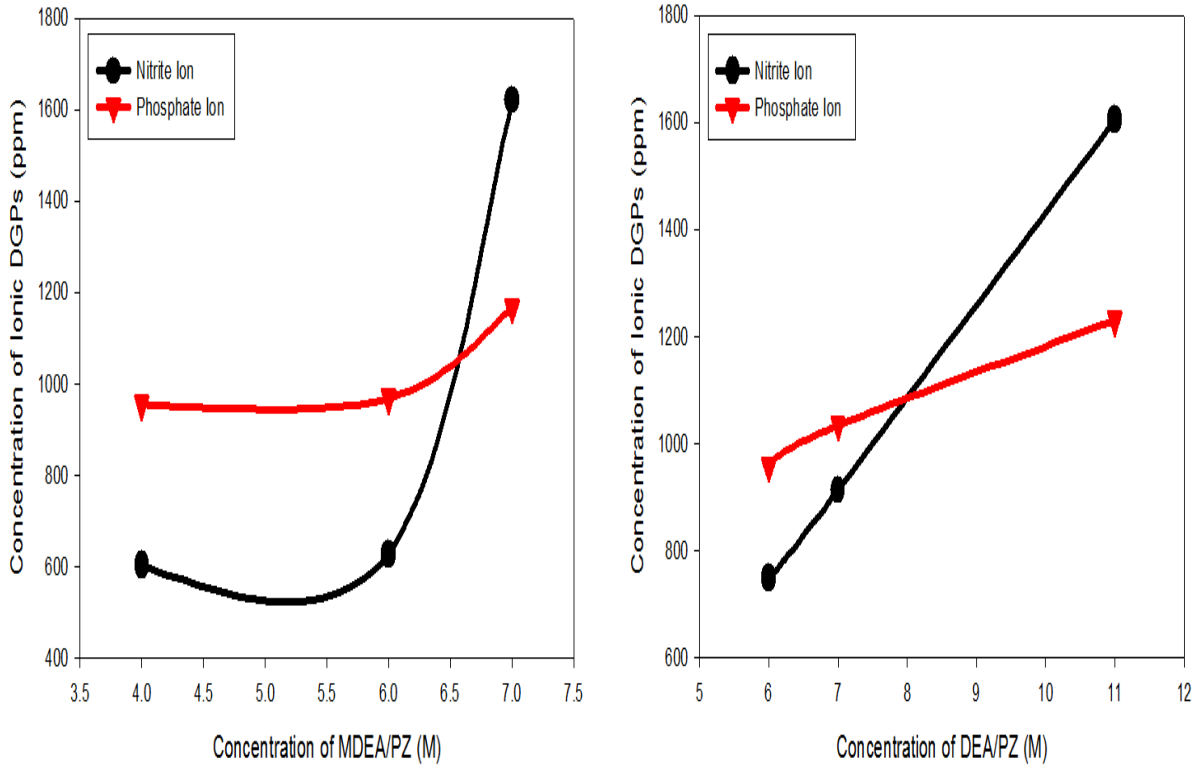


Figure 4.111: Variation of concentration of Ionic DGPs of activated alkanolamines identified by IC analysis.

Figure 4.112 represents the variation of concentration of ionic DGPs of activated and inactivated DEA and MDEA. The variation of concentartion of nitrite, phosphate and acetate ions are shown in the figure 4.112A for inactiavted DEA and MDEA. Since the concentartion of these DGPs are decreased with alkanolamine concentartion so it will decreases the slution's viscosity and density. The concentration of ionic degradtion products of activated DEA and MDEA are shown in the figure 4.112B. In this figure the concentration of phospahte and nitrite ions for DEA/PZ are shown in increased finally, but at 7M and 8M, concentartions are found decreased. On the other hand, in case of MDEA/PZ, nitrite and nitrate ions are decresed with amine concentration. Therefore, from this results it can be stated that, the ions or DGPs which are increased with amine concentration it will increase the density and viscosity of the solution.

In the figure 4.112A, the concentration of all ionic DGPs are decreased with increasing of amine concentration, only phosphate ion showed deviation at concentration level 4M in case of DEA. The highest concentration of phosphate and nitrite ions are found in the figure 4.112B for 11M diethanolamine solution, but at concentration level 8M which is found lowest. From this observation 8M activated DEA and MDEA were found lowest occuring of ionic DGPs which can be considered best because of high flow rate and low operating cost by considering density and viscosity. The ionic DGPs which are found low concentration these are not affect on the physical properties of amine solution. On the other hand those are found high concentrated these are affect amine solution and significantly increas viscosity, density, corrosion and decreas absorption capacity.

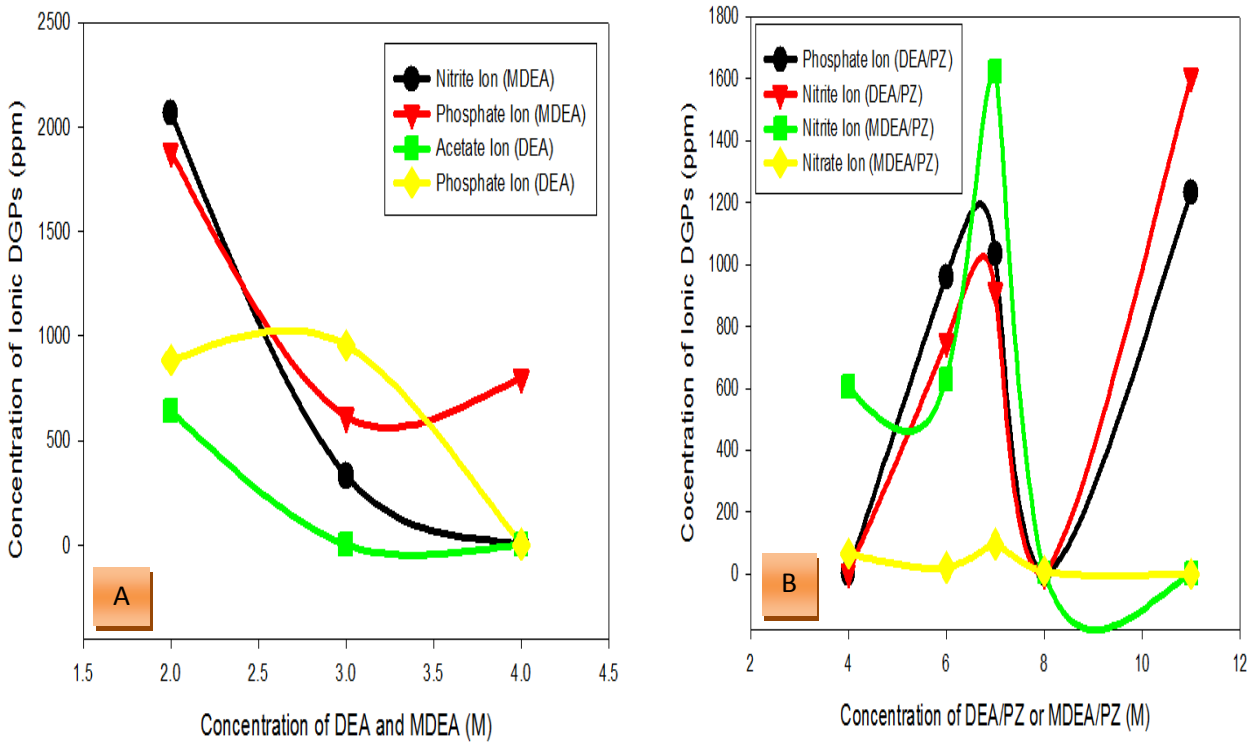


Figure 4.112: Variation of concentrations of Ionic DGPs of activated and inactivated alkanolamines identified by IC analysis.

CHAPTER 05

CONCLUSIONS AND RECOMMENDATIONS

CHAPTER 05: CONCLUSIONS AND RECOMMENDATIONS

This chapter details the key findings of this study on amine degradation induced by carbon dioxide at atmospheric conditions under true amine based absorption and stripping condition. The degraded samples were analyzed by HPLC–UV, GC-MS and IC methods in order to identify the degradation products (DGPs). Results are presented for five degradation system in activated and inactivated condition. Finally, recommendations are made for future work on amine degradation.

5.1 CONCLUSIONS

The conclusions were drawn for five degradation system in order to understand the effect of activator on alkanolamine degradation using PZ as activator. Two amines were used in this study these are diethanolamine (DEA) and methyldiethanolamine (MDEA).

5.1.1 Degradation System I: PZ+H_2O+CO_2

D01PZ1M and D02PZ2M of this degradation system are analyzed by HPLC (UV) method and identified degradation products are formamide, 2-(2-aminoethoxyethanol) and 2-methoxyethanol. In the IC analysis these two samples were analyzed were as acetate, nitrate, phosphate and ammonium ions were found as ionic degradation products. The DGPs are identified by GC-MS method for DO2PZ2M sample and which are Formamide, Ethylenediamine, N-formylpiperazine, formic acid and imodazole.

5.1.2 Degradation System II: DEA+H_2O+CO_2

Three different samples were prepared of this degradation system these are D03DEA2M, D04DEA3M and D05DEA4M. From the HPLC analysis the main degradation products were found to be formamide, 2-methoxyethanol, diethylenetriamine, 2-(2-aminoethoxy)-ethanol, triethanolamine, acetone, ethanol and Ethyl 1-piperazinecarboxylate. From the IC analysis ionic DGPs were found ammonium, acetate, nitrite and phosphate. GC-MS is only conducted for D05DEA4M of this degradation system and identified DGPs are

Formamide, N-(hydroxyethy1) ethylenediamine, Oxazolidone, 2-(2-aminoethoxy) ethanol, 2-amino-2-methyl-1-propanol, N,N-bis(hydroxyethy1)- ethylenediamine, Ethylurea, 2-methylaminoethanol, ethanol and acetone.

5.1.3 Degradation System III: DEA+PZ+H_2O+CO_2

D06DEA2MPZ1M activated sample of DEA is analyzed by HPLC-UV method and six DGPs are identified which are Formamide, 2-methoxyethanol, 2-(2-aminoethoxy)-ethanol, 1-(2-Aminoethyl)-piperazine, 1, 4-dimethylpiperazine and Ethyl-1-piperazinecarboxylate. The other two activated DEA samples are D07DEA2MPZ2M & D08DEA3MPZ2M shows four DGPs which are formamide, 2-methoxyethanol, 2-(2-aminoethoxy)-ethanol and Ethyl-1-piperazinecarboxylate. The last two activated samples of five are D09DEA4MPZ2M & D10DEA7MPZ2M shows the six common degradation products these are formamide, 2-methoxyethanol, 2-(2-aminoethoxy)-ethanol, 1-(2-Aminoethyl)-piperazine, 1, 4-dimethylpiperazine and Ethyl-1-piperazinecarboxylate.

Under this degradation system GC-MS is conducted for activated sample D10DEA10MPZ2M and the identified degradation products are twelve which are Formamide, 1,4-Bis(2-hydroxyethyl)piperazine, Oxazolidone, 1,4-Dimethylpiperazine, N,N-bis(hydroxyethy1)ethylenediamine, 2-dimethylaminoethanol, 1-(2-Aminoethyl)piperazine, Ethyl-1-piperazinecarboxylate, Acetic acid, Glycolic acid, Ethylurea and Acetone.

The most common ionic degradation products of these above mentioned samples are identified by IC methods and the identified degradation products are namely nitrite, nitrate, ammonium and phosphate.

5.1.4 Degradation System IV: MDEA+H_2O+CO_2

Three samples D11MDEA2M, D12MDEA3M and D13MDEA4M were prepared for this degradation system, both of these analyzed and found degradation products are namely formamide and 2-methoxyethanol. On the other hand identified ionic degradation products are nitrite, phosphate, acetate and ammonium. GC-MS method is conducted for high concentrated inactivated amine sample D13MDEA4M and the identified DGPs are 1, 4-Bis (2-hydroxyethyl)-piperazine, Bis-(2-hydroxypropyl) amine, Oxazolidone, 2-(2-aminoethoxy)ethanol, 2-Amino-2-methyl-1-propanol, 2-dimethylaminoethanol, Ethylurea, Glycolic acid, Acetal dehyde, Ethanol and Acetic acid.

5.1.5 Degradation System V: MDEA+PZ+H_2O+CO_2

Activated MDEA system comprises of five different samples namely these are D14MDEA2MPZ1M, D15MDEA2MPZ2M, D16MDEA3MPZ2M, D17MDEA4MPZ2M and D18MDEA7MPZ2M. MDEA was found very stable and high resistance over DEA even though activated DEA samples. The identified degradation products are formamide, 2-methoxyethanol and ethanol. From the IC analysis identified ionic degradation products are nitrate, nitrite, phosphate and acetate. From the GC-MS analysis for D18MDEA7MPZ2M sample there are eight DGPs are identified which are 1-Methyl piperazine, 1, 4-Bis(2-hydroxyethyl)piperazine, Bis(2-hydroxypropyl) amine, N, N- dimethyl piperazine, 2-Amino-2-methyl-1-propanol, 2-dimethylaminoethanol, 1-(2-aminoethyl) piperazine and ethanol.

5.1.6 Density and Viscosity

Density and viscosity of activated and inactivated alkanolamine samples are measures at 30 ˚C, 55 ˚C and 100 ˚C temperatures. From this result it is stated that, both parameters are decreased when the temperatures are inceased and when the temperatures are increased the opposite trends are observed.

The effect of amine concentration on density and viscosity are also studied for several concentrations and the final result is briefly stated that, the increasing of amine concentration significantly increases the density and viscosity. At higher concentration of amine solution, both parameters i.e. density and viscosity are found high. The same experiences are found for activated and inactivated samples.

5.2 Recommendations

- In this study, the high performance liquid chromatography (HPLC) technique was used in analyzing the degraded samples of activated and inactivated DEA and MDEA. It is recommended that other techniques such as GC-MS and CE-DAD be used for the same analysis.
- During the analysis we used single column in case of HPLC and IC analysis. In order to get more information dual column is recommended for further analysis.
- In the present work identification of degradation products is only carried out, to understand degradation phenomenon its kinetics, modeling and mechanism is recommended for future research on this fields.
- The whole experiment was conducted under absorption and stripping condition where as the temperature was settled 55 and 100 ˚C for absorption and stripping condition respectively. The range of temperature for stripping is 100-120 ˚C. The experiment to be conducted at 120 ˚C for full understanding degradation phenomenon.
- The degradation experiment was done at low atmospheric condition so future research to be conducted under high pressure.

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APPENDIX

APPENDIX A: LIST OF CHEMICALS USED IN THIS WORK

Si.	Chemicals /ID	P. ID	Company	Formula	Synonym	Molecular Wet.
1	Bicine	B3876	Sigma Al.	$C_6H_{13}NO_4$	N,N-Bis(2-hydroxyethyl)glycine	163.17
2	2-Oxazolidone	75793	Sigma Al.	$C_3H_5NO_2$	-	87.08
3	1, 4-Bis(2-hydroxyethyl)piperazine	B45402	Sigma Al.	$C_8H_{18}N_2O_2$	1,4-Piperazinediethanol	174.24
4	1-(2-Aminoethyl)piperazine	A55209	Sigma Al.	$C_6H_{15}N_3$	2-Piperazinoethylamine	129.20
5	1-[2-(2-Hydroxyethoxy)ethyl]piperazine	331260	Sigma Al.	$C_8H_{18}N_2O_2$	2-[2-(1-Piperazinyl)ethoxy]ethanol	174.24
6	N-Acetylethanolamine	100455	Sigma Al.	$CH_3CONHCH_2CH_2OH$	N-(2-Hydroxyethyl)acetamide	103.12
7	N,N'-Bis(2-hydroxyethyl) ethylenediamine (BHEED)	268879	Sigma Al.	$HOCH_2CH_2NHCH_2CH_2NHCH_2CH_2OH$	2,2′-(Ethylenediimino)diethanol	148.20
8	2-(Ethylamino)ethanol	471461	Sigma Al.	$C_2H_5NHCH_2CH_2OH$	N-Ethylethanolamine	89.14
9	Imidazole	56750	Sigma Al.	$C_3H_4N_2$	1,3-Diaza-2,4-cyclopentadiene; Glyoxaline	68.08
10	Piperidine	P5881	Sigma Al.	$C_5H_{11}N$	Hexahydropyridine	85.15
11	Diethylenetriamine	15918	Sigma Al.	$(NH_2CH_2CH_2)_2NH$	2,2′-Diaminodiethylamine, 2,2′-Iminodiethylamine, Bis(2-aminoethyl)amine	103.17
12	N-(2-Hydroxyethyl)ethylenediamine (HEED)	127582	Sigma Al.	$NH_2CH_2CH_2NHCH_2CH_2OH$	2-(2-Aminoethylamino)ethanol, N-(2-Aminoethyl)ethanolamine	104.15
13	1-(2-Aminoethyl)piperazine	A55209	Sigma Al.	$C_6H_{15}N_3$	2-Piperazinoethylamine	129.20
14	1-Formylpiperazine technical	47727	Sigma Al.	$C_5H_{10}N_2O$	Piperazine-1-carboxaldehyde	114.15
15	Ethyl 1-piperazinecarboxylate	02630	Sigma Al.	$C_7H_{14}N_2O_2$	1-Ethoxycarbonylpiperazine, Piperazine-1-carboxylic acid ethyl ester	158.20
16	2-Methoxyethanol anhydrous	284467	Sigma Al.	$CH_3OCH_2CH_2OH$	Ethylene glycol monomethyl ether, Methyl Cellosolve, Methyl glycol	76.09
17	Formamide	F9037	Sigma Al.	$HCONH_2$	Amide C_1, Formic amide	45.04
18	1,4-Dimethylpiperazine	D179302	Sigma Al.	$C_6H_{14}N_2$	-	114.19
19	1-Methylimidazole	336092	Sigma Al.	$C_4H_6N_2$	-	82.10
20	2-Methylimidazole	67570	Sigma Al.	$C_4H_6N_2$	2-Methylglyoxaline	82.10

APPENDIX A: CONTINUED

Si.	Chemicals /ID	P. ID	Company	Formula	Synonym	Molecular Wet.
21	4(5)-Methylimidazole	67580	Sigma Al.	$C_4H_6N_2$	-	82.10
22	2-Dimethylaminoethanol (DMAE)	38990	Sigma Al.	$(CH_3)_2NCH_2CH_2OH$	N,N-Dimethyl-2-hydroxyethylamine, N,N-Dimethylethanolamine	89.14
23	N-Methyldiethanolamine (MDEA)	M42203	Merck.	$CH_3N(CH_2CH_2OH)_2$	2,2′-Methyliminodiethanol, N,N-Bis(2-hydroxyethyl) methylamine, N-methyl-2,2'-iminodiethanol	119.16
24	Ethylene glycol (EG)	03747	Sigma Al.	$HOCH_2CH_2OH$	1,2-Ethanediol	62.07
25	Diethanolamine (DEA)	31589	Merck.	$HN(CH_2CH_2OH)_2$	2,2′-Iminodiethanol, Bis(2-hydroxyethyl)amine	105.14
26	Triethanolamine (TEA)	90279	Sigma Al.	$(HOCH_2CH_2)_3N$	2,2′,2″-Nitrilotriethanol, Tris(2-hydroxyethyl)amine	149.19
27	2-(2-aminoethoxy)ethanol (DGA)	A54059	Sigma Al.	$NH_2CH_2CH_2OCH_2CH_2OH$	Diethylene glycolamine	105.14
28	Bis(2-hydroxypropyl) amine (DIPA)	14960	Sigma Al.	$NH[CH_2CH(OH)CH_3]_2$	1,1′-Iminodi-2-propanol, Diisopropanolamine	133.19
29	2-(Methylamino)ethanol (MMEA)	15770	Sigma Al.	$CH_3NHCH_2CH_2OH$	N-Methylethanolamine	75.11
30	Ethyldiethanolamine (EDEA)	112062	Merck.	$(HOCH_2CH_2)_2NC_2H_5$	2,2′-Ethyliminodiethanol	133.19
31	1-[3-(Dimethylamino)propyl]piperazine	94663	Sigma Al.	$C_9H_{21}N_3$	N,N-Dimethyl-1-piperazinepropanamine, N,N-Dimethyl-3-piperazinopropylamine	171.28
32	1-[2-(Dimethylamino)ethyl]piperazine	74328	Sigma Al.	$C_8H_{19}N_3$	N,N-Dimethyl-1-piperazineethanamine, N,N-Dimethyl-2-piperazinoethylamine	157.26
33	N,N-Dimethylformamide	D4551	Sigma Al.	$HCON(CH_3)_2$	DMF	73.09
34	2-Methoxyethanol	284467	Sigma Al.	$CH_3OCH_2CH_2OH$	Ethylene glycol monomethyl ether, Methyl Cellosolve, Methyl glycol	76.09
35	N,N'-Bis(hydroxyethyl)-ethylenediamine	268879	Sigma Al.	$(HOC_2H_4)_2N\text{-}C_2H_4\text{-}NH_2$	2,2′-(Ethylenediimino)diethanol	148.20
36	Monoetanolamine (MEA)	411000	Merck.	$NH_2CH_2CH_2OH$	2-Aminoethanol, 2-Aminoethyl alcohol, Ethanolamine	61.08
37	N-(hydroxyethyl) ethyleneimine (HEM)	106909	Sigma Al.	C_4H_9NO	1-(2-Hydroxyethyl) ethylenimine	87.12
38	1-(2-Hydroxyethyl)piperazine	H28807	Sigma Al.	$C_6H_{14}N_2O$	2-Piperazinoethanol, Piperazine-1-ethanol	130.19
39	1-Methylpiperazine	68810	Sigma Al.	$C_5H_{12}N_2$	…..	100.16
40	Piperazine	80621	Merck	$C_4H_{10}N_2$	1,4-Diazacyclohexane, Diethylenediamine	86.14

APPENDIX A: CONTINUED

Si.	Chemicals /ID	P. ID/CAS	Company	Formula	Synonym	Molecular Wet.
41	Acetone	414989	Sigma Al.	C_3H_8O	Dimethylketone	58.08
42	Ethanol	362808	Sigma Al.	C_2H_6O	Ethyl alcohol, Reagent alcohol, Ethyl alcohol	46.07
43	Ethylenimine, Oligomer mixture	-	Sigma Al.	--	--	M_n ~ 423.00
44	1,2,4,5-Benzenetetracarboxylic anhydride	89-32-7	Sigma Al.	$C_{10}H_2O_6$	Pyromellitic dianhydride; Benzene-1,2,4,5-tetracarboxylic dianhydride; PMDA	218.12
45	N, N-Dimethylurea	D6254	Sigma Al.	$(CH_3NH)_2CO$	1,3-Dimethylurea	88.11
46	2-Amino-2-methyl-1-propanol	08580	Sigma Al.	$(CH_3)_2C(NH_2)CH_2OH$	β-Aminoisobutyl alcohol, AMP 100, AMP 75, AMP 90, AMP	89.14
47	Carbon Dioxide	--	Mox Pvt. Lt.	CO_2	--	44.00
48	Nitrogen	--	Mox Pvt. Lt.	N_2	--	28.00
49	Barium Chloride	10361-37-2	Merck	$BaCl_2$	--	244.28
50	Hydrochloric Acid	7647-01-0	Merck	HCl	--	36.46
51	Sodium Hydroxide	1310-73-2	Merck	NaOH	--	40
52	Potassium Hydroxide	1310-58-3	Merck	KOH	--	56.11
53	2,4-Phenyl Hydrazine	119-26-6	Sigma Ald.	$(O_2N)_2C_6H_3NHNH_2$	2,4-DNPH	198.14
54	Liquid soap	--	--	--	--	--
55	Benzene	71-43-2	Merck	C_6H_6	--	78.11
56	Potassiumdihydrogen Phosphate	7778-77-0	Fisher	KH_2PO_4	Potassium Phisphate Monobasic	136.09

APPENDIX B: RETENTION TIME OF SELECTED ANALYTICAL STANSARDS FOR HPLC-UV

Si.	Chemicals	ID/PL	Formula	Synonym	Molecular Wet.	R. Time
1	1-(2-Aminoethyl)piperazine	4	$C_6H_{15}N_3$	2-Piperazinoethylamine	129.20	5.638
2	Diethylenetriamine	11	$(NH_2CH_2CH_2)_2NH$	2,2′-Diaminodiethylamine, 2,2′-Iminodiethylamine, Bis(2-aminoethyl)amine	103.17	4.279
3	N-(2-Hydroxyethyl)ethylenediamine (HEED)	12	$NH_2CH_2CH_2NHCH_2CH_2OH$	2-(2-Aminoethylamino)ethanol, N-(2-Aminoethyl)ethanolamine	104.15	5.119
4	Ethyl 1-piperazinecarboxylate	15	$C_7H_{14}N_2O_2$	1-Ethoxycarbonylpiperazine, Piperazine-1-carboxylic acid ethyl ester	158.20	7.776
5	Formamide	17	$HCONH_2$	Amide C_1, Formic amide	45.04	2.996
6	1,4-Dimethylpiperazine	18	$C_6H_{14}N_2$	-------	114.19	6.754
7	N-Methyldiethanolamine (MDEA)	23	$CH_3N(CH_2CH_2OH)_2$	2,2′-Methyliminodiethanol, N,N-Bis(2-hydroxyethyl) methylamine, N-methyl-2,2'-iminodiethanol	119.16	4.911
8	Ethylene glycol (EG)	24	$HOCH_2CH_2OH$	1,2-Ethanediol	62.07	3.176
9	Diethanolamine (DEA)	25	$HN(CH_2CH_2OH)_2$	2,2′-Iminodiethanol, Bis(2-hydroxyethyl)amine	105.14	4.437
10	Triethanolamine (TEA)	26	$(HOCH_2CH_2)_3N$	2,2′,2″-Nitrilotriethanol, Tris(2-hydroxyethyl)amine	149.19	5.040
11	2-(2-aminoethoxy)ethanol (DGA)	27	$NH_2CH_2CH_2OCH_2CH_2OH$	Diethylene glycolamine	105.14	4.772
12	1-[3-(Dimethylamino)propyl]piperazine	31	$C_9H_{21}N_3$	N,N-Dimethyl-1-piperazinepropanamine, N,N-Dimethyl-3-piperazinopropylamine	171.28	4.567
13	1-[2-(Dimethylamino)ethyl]piperazine	32	$C_8H_{19}N_3$	N,N-Dimethyl-1-piperazineethanamine, N,N-Dimethyl-2-piperazinoethylamine	157.26	4.627
14	2-Methoxyethanol	34	$CH_3OCH_2CH_2OH$	Ethylene glycol monomethyl ether, Methyl Cellosolve, Methyl glycol	76.09	3.745
15	Monoetanolamine (MEA)	36	$NH_2CH_2CH_2OH$	2-Aminoethanol, 2-Aminoethyl alcohol, Ethanolamine	61.08	4.824
16	1-(2-Hydroxyethyl)piperazine	42	$C_6H_{14}N_2O$	2-Piperazinoethanol, Piperazine-1-ethanol	130.19	4.912
17	1-Methylpiperazine	43	$C_5H_{12}N_2$	…..	100.16	5.791
18	Piperazine	44	$C_4H_{10}N_2$	1,4-Diazacyclohexane, Diethylenediamine	86.14	5.158
19	Acetone	45	C_3H_6O	Dimethylketone	58.08	6.092
20	Ethanol	46	C_2H_6O	Ethyl alcohol, Reagent alcohol, Ethyl alcohol	46.07	4.117
21	2-Amino-2-methyl-1-propanol	50	$(CH_3)_2C(NH_2)CH_2OH$	β-Aminoisobutyl alcohol, AMP 100, AMP 75, AMP 90, AMP	89.14	4.991
22	Water	51	H_2O	-------	18.00	2.601

APPENDIX C: RETENTION TIME OF SELECTED ANALYTICAL STANSARDS FOR GC-MS

Si.	Chemicals /ID	ID/PL	Formula	Synonym	Molecular Wet.	R. Time
1	Bicine	1	$C_6H_{13}NO_4$	N,N-Bis(2-hydroxyethyl)glycine	163.17	3.125
2	2-Oxazolidone (OZD)	2	$C_3H_5NO_2$	--	87.08	7.925
3	1, 4-Bis(2-hydroxyethyl)piperazine (BHEP)	3	$C_8H_{18}N_2O_2$	1,4-Piperazinediethanol	174.24	5.102
4	1-(2-Aminoethyl)piperazine (AEP)	4	$C_6H_{15}N_3$	2-Piperazinoethylamine	129.20	11.564
5	1-[2-(2-Hydroxyethoxy)ethyl]piperazine	5	$C_8H_{18}N_2O_2$	2-[2-(1-Piperazinyl)ethoxy]ethanol	174.24	3.789
6	N,N'-Bis(2-hydroxyethyl) ethylenediamine (BHEED)	7	$HOCH_2CH_2NHCH_2CH_2NHCH_2CH_2OH$	2,2′-(Ethylenediimino)diethanol	148.20	11.087
7	Imidazole	9	$C_3H_4N_2$	1,3-Diaza-2,4-cyclopentadiene; Glyoxaline	68.08	21.1891
8	Piperidine	10	$C_5H_{11}N$	Hexahydropyridine	85.15	16.547
9	N-(2-Hydroxyethyl)ethylenediamine (HEED)	12	$NH_2CH_2CH_2NHCH_2CH_2OH$	2-(2-Aminoethylamino)ethanol, N-(2-Aminoethyl)ethanolamine	104.15	5.657
10	Formamide (FM)	17	$HCONH_2$	Amide C_1, Formic amide	45.04	3.534
11	1,4-Dimethylpiperazine (DMP)	18	$C_6H_{14}N_2$	-	114.19	8.003
12	2-Dimethylaminoethanol (DMAE)	22	$(CH_3)_2NCH_2CH_2OH$	N,N-Dimethyl-2-hydroxyethylamine, N,N-Dimethylethanolamine	89.14	11.201
13	N-Methyldiethanolamine (MDEA)	23	$CH_3N(CH_2CH_2OH)_2$	2,2′-Methyliminodiethanol, N,N-Bis(2-hydroxyethyl) methylamine, N-methyl-2,2'-iminodiethanol	119.16	15.532
14	Ethylene glycol (EG)	24	$HOCH_2CH_2OH$	1,2-Ethanediol	62.07	2.897
15	Diethanolamine (DEA)	25	$HN(CH_2CH_2OH)_2$	2,2′-Iminodiethanol, Bis(2-hydroxyethyl)amine	105.14	10.928
16	2-(2-aminoethoxy)ethanol (DGA)	27	$NH_2CH_2CH_2OCH_2CH_2OH$	Diethylene glycolamine	105.14	9.258
17	Bis(2-hydroxypropyl) amine (DIPA)	28	$NH[CH_2CH(OH)CH_3]_2$	1,1′-Iminodi-2-propanol, Diisopropanolamine	133.19	6.125
18	2-(Methylamino)ethanol (MMEA)	29	$CH_3NHCH_2CH_2OH$	N-Methylethanolamine	75.11	2.698
19	Ethyldiethanolamine (EDEA)	30	$(HOCH_2CH_2)_2NC_2H_5$	2,2′-Ethyliminodiethanol	133.19	2.312
20	1-[3-(Dimethylamino)propyl]piperazine	31	$C_9H_{21}N_3$	N,N-Dimethyl-1-piperazinepropanamine, N,N-Dimethyl-3-piperazinopropylamine	171.28	2.541

APPENDIX C: CONTINUED

Si.	Chemicals /ID	ID/PL	Formula	Synonym	Molecular Wet.	R. Time
21	1-[2-(Dimethylamino)ethyl]piperazine	32	$C_8H_{19}N_3$	N,N-Dimethyl-1-piperazineethanamine, N,N-Dimethyl-2-piperazinoethylamine	157.26	1.240
22	N, N'-Bis(hydroxyethyl)-ethylenediamine	35	$(HOC_2H_4)_2N\text{-}C_2H_4\text{-}NH_2$	2,2′-(Ethylenediimino)diethanol	148.20	1.997
23	Monoetanolamine (MEA)	36	$NH_2CH_2CH_2OH$	2-Aminoethanol, 2-Aminoethyl alcohol, Ethanolamine	61.08	1.521
24	N-(hydroxyethyl) ethyleneimine (HEM)	41	C_4H_9NO	1-(2-Hydroxyethyl) ethylenimine	87.12	1.751
25	1-(2-Hydroxyethyl)piperazine (HEP)	42	$C_6H_{14}N_2O$	2-Piperazinoethanol, Piperazine-1-ethanol	130.19	17.231
26	1-Methylpiperazine (MP)	43	$C_5H_{12}N_2$	…..	100.16	5.087
27	Piperazine (PZ)	44	$C_4H_{10}N_2$	1,4-Diazacyclohexane, Diethylenediamine	86.14	16.012
28	2-Amino-2-methyl-1-propanol (AMP)	50	$(CH_3)_2C(NH_2)CH_2OH$	β-Aminoisobutyl alcohol, AMP 100, AMP 75, AMP 90	89.14	9.913
29	Ethyl Urea (EU)	54	$C_3H_8N_2O$	--	90.68	13.125
30	2-Methylaminoethanol (MAE)	55	$(CH_3)NCH_2CH_2OH$	**N-Methylethanolamine**	75.11	14.201
31	Ethyl 1-piperazinecarboxylate (EPC)	15	$C_7H_{14}N_2O_2$	1-Ethoxycarbonylpiperazine, Piperazine-1-carboxylic acid ethyl ester	158.20	18.199
32	Glycolic acid (GA)	56	$HOCH_2COOH$	**Hydroxyacetic acid**	76.05	15.013
33	Ethylenediamine	52	$C_2H_8N_2$	**1,2-Diaminoethane**	60.10	5.019
34	N-Formylpiperazine	53	$C_5H_{10}N_2O$	**Piperazine-1-carboxaldehyde**	114.15	8.712

APPENDIX D: ANALYTICAL STANDARDS AND REAGENTS FOR ION CHROMATOGRAPHY (IC)

Chemicals	Mol. Formula	Mol. Wet.	Company	CAS No.	Assay (%)
UPW	H_2O	18.00	Self Produced	--	--
Ammonium oxalate	$C_2O_4(NH_4)_2$	142.11	Sigma-Aldrich	6009-70-7	99.00
Sulphuric acid	H_2SO_4	98.08	Sigma-Aldrich	7664-93-9	95-98
Hydrochloric acid	HCl	36.46	Sigma-Aldrich	7647-01-0	37.00
Acetic acid	CH_3COOH	60.05	Sigma-Aldrich	64-19-7	>99.70
Sodium acetate	CH_3COONa	82.03	Sigma-Aldrich	127-09-3	99.00
Sodium nitrite	$NaNO_2$	69.00	Sigma-Aldrich	7632-00-0	97.00
Sodiumpropionate	CH_3CH_2COONa	96.06	Sigma-Aldrich	137-40-6	98.98
Glycolate	$HOCH_2COO$	75.05	Fluka	7732-18-5	99.85
Formate	HCOOH	46.03	Fluka	64-18-6	98.50
Nitrate	NO_3	52.00	Fluka	74246	99.75
Phosphate	Na_2HPO_4	141.96	Fluka	7558-79-4	98.95
Propionate	CH_3CH_2COO	74.08	Sigma-Aldrich	79-09-4	98.98
Butyric acid	CH_3CH_2COO	88.11	Fluka	107-92-6	99.88
Valeric acid	$CH_3(CH_2)_3COOH$	102.13	Fluka	109-52-4	99.85

APPENDIX E: VARIATION OF pH FOR VIRGIN & DEGRADED SOLUTIONS

T. Ex. Run	Sample Code	Amine (AM)	[AM]	Activator (AC)	[AC]	CY-0 pH-Vs	CY-01 pH-Rs	CY-06 pH-Ls
D01	D01PZ1M	--	--	PZ	1M	11.61	7.71	8.93
D02	D02PZ2M	--	--	PZ	2M	11.70	7.83	8.8
D03	D03DEA2M	DEA	2M	--	--	11.11	8.05	8.21
D04	D04DEA3M	DEA	3M	--	--	11.56	8.07	8.45
D05	D05DEA4M	DEA	4M	--	--	11.71	8.01	8.51
D06	D06DEA2MPZ1M	DEA	2M	PZ	1M	11.86	8.04	8.53
D07	D07DEA2MPZ2M	DEA	2M	PZ	2M	12.24	8.07	8.66
D08	D08DEA3MPZ2M	DEA	3M	PZ	2M	12.06	8.18	8.69
D09	D09DEA4MPZ2M	DEA	4M	PZ	2M	11.88	8.38	9.19
D10	D10DEA7MPZ2M	DEA	7M	PZ	2M	11.89	8.41	9.70
D11	D11MDEA2M	MDEA	2M	--	--	11.40	8.13	9.09
D12	D12MDEA3M	MDEA	3M	--	--	10.87	8.39	8.87
D13	D13MDEA4M	MDEA	4M	--	--	10.64	8.52	8.74
D14	D14MDEA2MPZ1M	MDEA	2M	PZ	1M	11.52	8.32	8.70
D15	D15MDEA2MPZ2M	MDEA	2M	PZ	2M	11.70	9.05	8.56
D16	D16MDEA3MPZ2M	MDEA	3M	PZ	2M	11.62	8.62	9.08
D17	D17MDEA4MPZ2M	MDEA	4M	PZ	2M	11.65	8.40	9.12
D18	D18MDEA7MPZ2M	MDEA	7M	PZ	2M	11.04	8.97	9.45

APPENDIX F: MEASUREMENT OF CARBON DIOXIDE LOADING OF DEGRADED AMINE SOLUTIONS

T. Ex. Run	Sample Code	Amine (AM)	[AM]	Activator (AC)	[AC]	CY-01 Rα	CY-06 Lα
D01	D01PZ1M	--	--	PZ	1M	0.60	0.40
D02	D02PZ2M	--	--	PZ	2M	0.80	0.30
D03	D03DEA2M	DEA	2M	--	--	0.58	0.28
D04	D04DEA3M	DEA	3M	--	--	0.56	0.27
D05	D05DEA4M	DEA	4M	--	--	0.59	0.34
D06	D06DEA2MPZ1M	DEA	2M	PZ	1M	0.70	0.40
D07	D07DEA2MPZ2M	DEA	2M	PZ	2M	0.70	0.30
D08	D08DEA3MPZ2M	DEA	3M	PZ	2M	0.72	0.32
D09	D09DEA4MPZ2M	DEA	4M	PZ	2M	0.71	0.30
D10	D10DEA7MPZ2M	DEA	7M	PZ	2M	0.73	0.30
D11	D11MDEA2M	MDEA	2M	--	--	0.18	0.10
D12	D12MDEA3M	MDEA	3M	--	--	0.20	0.10
D13	D13MDEA4M	MDEA	4M	--	--	0.20	0.10
D14	D14MDEA2MPZ1M	MDEA	2M	PZ	1M	0.45	0.20
D15	D15MDEA2MPZ2M	MDEA	2M	PZ	2M	0.48	0.20
D16	D16MDEA3MPZ2M	MDEA	3M	PZ	2M	0.50	0.20
D17	D17MDEA4MPZ2M	MDEA	4M	PZ	2M	0.50	0.20
D18	D18MDEA7MPZ2M	MDEA	7M	PZ	2M	0.50	0.23

APPENDIX G: MEASUREMENT OF DENSITIES OF DEGRADED AMINE SOLUTIONS

Ex. Run	Sample Code	Amine (AM)	[AM]	Activator (AC)	[AC]	CY-00 VS, T-30 ^{0}C	CY-06, LS T-30 ˚C	CY-06, LS T-55 ˚C	CY-06, LS T-100 ˚C
D01	D01PZ1M	--	--	PZ	1M	1002.214	1009.6100	1003.1400	992.2120
D02	D02PZ2M	--	--	PZ	2M	1007.564	1011.5900	1006.3200	998.3610
D03	D03DEA2M	DEA	2M	--	--	1004.325	1014.3500	1010.2700	1000.2120
D04	D04DEA3M	DEA	3M	--	--	1018.362	1024.6000	1012.3800	1002.4120
D05	D05DEA4M	DEA	4M	--	--	1026.641	1034.7000	1014.3000	1004.0400
D06	D06DEA2MPZ1M	DEA	2M	PZ	1M	1019.624	1021.8300	1028.6700	1012.3200
D07	D07DEA2MPZ2M	DEA	2M	PZ	2M	1025.291	1031.9600	1037.5600	1023.2000
D08	D08DEA3MPZ2M	DEA	3M	PZ	2M	1029.456	1043.9200	1046.3400	1031.2500
D09	D09DEA4MPZ2M	DEA	4M	PZ	2M	1041.369	1078.5400	1058.5600	1039.5400
D10	D10DEA7MPZ2M	DEA	7M	PZ	2M	1072.658	1117.1100	1069.2400	1054.2600
D11	D11MDEA2M	MDEA	2M	--	--	1007.874	1013.0900	1006.2000	1001.3500
D12	D12MDEA3M	MDEA	3M	--	--	1021.974	1026.4900	1015.0200	1009.2600
D13	D13MDEA4M	MDEA	4M	--	--	1030.685	1036.6400	1024.0400	1018.7400
D14	D14MDEA2MPZ1M	MDEA	2M	PZ	1M	1024.201	1045.2300	1010.6800	1002.6200
D15	D15MDEA2MPZ2M	MDEA	2M	PZ	2M	1027.235	1056.2411	1019.4500	1012.3800
D16	D16MDEA3MPZ2M	MDEA	3M	PZ	2M	1037.865	1064.2525	1026.9100	1020.1400
D17	D17MDEA4MPZ2M	MDEA	4M	PZ	2M	1047.447	1087.8200	1057.4500	1027.8600
D18	D18MDEA7MPZ2M	MDEA	7M	PZ	2M	1084.451	1135.8300	1098.2400	1033.6200

Note: CY-Cycle, VS-Virgin Alkanolamine Solution, LS-Lean Carbonated Solutions, T-Temperature

APPENDIX H: MEASUREMENT OF VISCOSITIES (μ) OF DEGRADED AMINE SOLUTIONS

T. Ex. Run	Sample Code	Amine (AM)	[AM]	Activator (AC)	[AC]	CY-00 VS	CY-06, LS T-30˚C	CY-06, LS T-55 ˚C	CY-06, LS T-100 ˚C
D01	D01PZ1M	--	--	PZ	1M	1.127	1.9800	1.4800	1.1200
D02	D02PZ2M	--	--	PZ	2M	1.456	2.1600	1.9200	1.3200
D03	D03DEA2M	DEA	2M	--	--	1.745	1.9500	1.4500	1.1000
D04	D04DEA3M	DEA	3M	--	--	2.852	3.0000	2.7400	1.6200
D05	D05DEA4M	DEA	4M	--	--	3.984	4.9500	3.4300	2.3000
D06	D06DEA2MPZ1M	DEA	2M	PZ	1M	2.856	3.2100	2.8000	1.6600
D07	D07DEA2MPZ2M	DEA	2M	PZ	2M	4.321	5.8800	4.2800	2.8100
D08	D08DEA3MPZ2M	DEA	3M	PZ	2M	8.652	10.5900	7.9400	6.2800
D09	D09DEA4MPZ2M	DEA	4M	PZ	2M	12.654	15.4300	11.5600	8.1900
D10	D10DEA7MPZ2M	DEA	7M	PZ	2M	28.124	32.9900	26.8800	19.470
D11	D11MDEA2M	MDEA	2M	--	--	2.288	2.2500	1.7600	1.2000
D12	D12MDEA3M	MDEA	3M	--	--	3.948	3.7800	2.9800	1.9200
D13	D13MDEA4M	MDEA	4M	--	--	7.782	7.0500	5.2300	3.7000
D14	D14MDEA2MPZ1M	MDEA	2M	PZ	1M	3.905	4.3500	3.3200	2.2000
D15	D15MDEA2MPZ2M	MDEA	2M	PZ	2M	4.102	8.2600	6.8700	4.1300
D16	D16MDEA3MPZ2M	MDEA	3M	PZ	2M	9.230	14.0700	10.7600	7.8600
D17	D17MDEA4MPZ2M	MDEA	4M	PZ	2M	20.062	27.6200	22.3600	12.6900
D18	D18MDEA7MPZ2M	MDEA	7M	PZ	2M	32.652	52.6200	44.5800	27.9300

Note: CY-Cycle, VS-Virgin Alkanolamine Solution, LS-Lean Carbonated Solutions, T-Temperature

APPENDIX I: CHROMATOGRAMS OF IC STANDARDS WITH RETENTION TIME

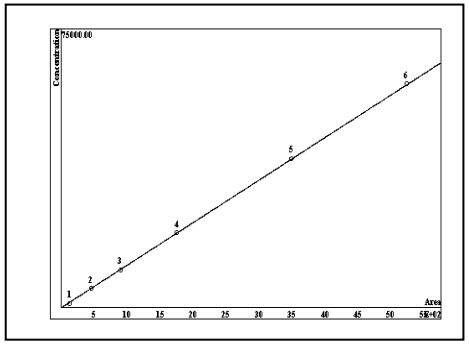

Fig. A1

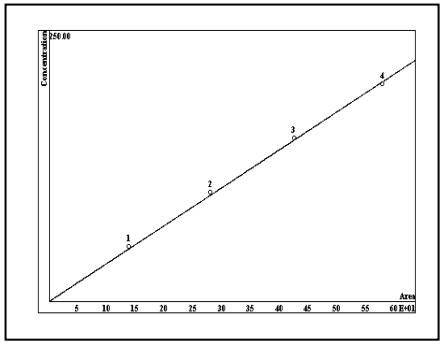

Fig. A2

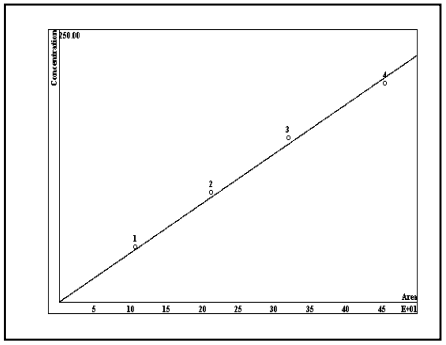

Fig. A3

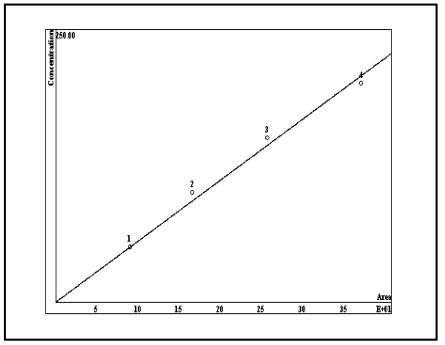

Fig. A4

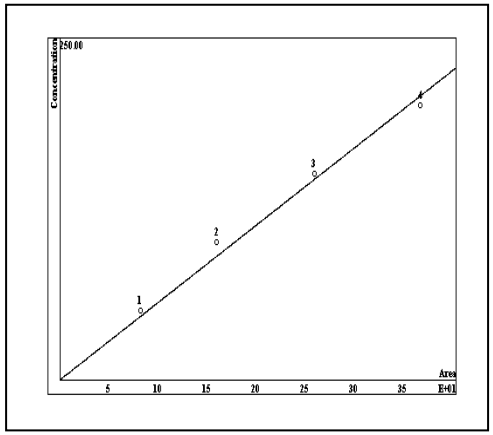

Fig. A5

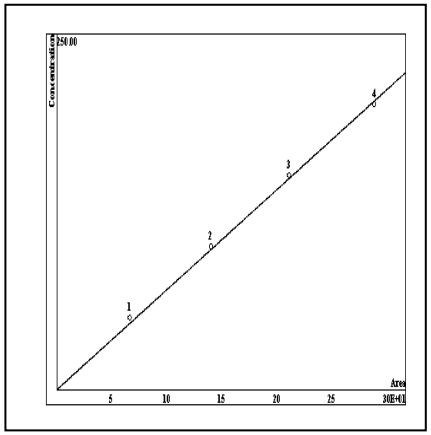

Fig. A6

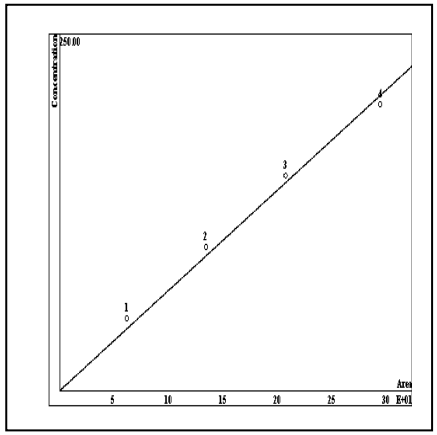

Fig. A7

Fig. A1: IC standard calibration curve for ammonium
Fig. A2: IC standard calibration curve for acetate
Fig. A3: IC standard calibration curve for propionate
Fig. A4: IC standard calibration curve for butyrate
Fig. A5: IC standard calibration curve for nitrate
Fig. A6: IC standard calibration curve for nitrite
Fig. A7: IC standard calibration curve for valerate

Figure Captions

APPENDIX J: PUBLICATIONS RELATED TO THE PRESENT WORK

Research Articles

- **M. S. Islam**, R. Yusoff, B. S. Ali, M. N. Islam, M. H. Chakrabarti. Degradation studies of amines and alkanolamines during sour gas treatment process, International Journal of the Physical Sciences, 2011, 6(1): 5883-5896 **[ISI Cited Publication, Q2]**

- **Md. Sakinul Islam**, Brahim Si Ali*, Rozita Yusoff. Comparative Study on degradation studies of Diethanolamine induced by carbon dioxide (To be Submitted in the Journal of Industrial and Engineering Chemistry, ISI Cited Publication)

Conferences Presentation

Md. Sakinul Islam, Brahim Si Ali*, Rozita Yusoff, Mohammad Harun Chakrabarti. Identification of Products Resulting from Carbon Dioxide Induced Degradation of Diethanolamine During Sour Gas Sweetening Process. AUN/SEED-Net, the 4th Regional Conference on Chemical Engineering, held on 9-10 February, 2012, pp. 99 (Paper ID Sep. 05).

Md. Sakinul Islam, Rozita Yusoff, Brahim Si Ali*, Degradation Reaction Mechanism of Amines and Alkanolamines in Sour Gas Processing Plant, Asia Pacific Offshore Conference -2010, (APOC 2010), held on 13-14 December, 2010, organized by UTM, Malaysia.

Md. Sakinul Islam, Rozita Yusoff, Brahim Si Ali*, Role of acids in the degradation of alkanolamines during CO_2 and H_2S removal process, International conference on marine technology (MARTEC 2010; ISSN-22203117), held on 11-12 December, 2010, Dhaka, Bangladesh, Abstract no MARTEC-119, pp. 241-247.

Md. Sakinul Islam, Rozita Yusoff, Brahim Si Ali*, Degradation Studies of Amines and Alkanolamines During Sour Gas Absorption and Stripping System in the natural gas industry, Third International Conference on Science & Technology (ICSTIE 2010), UiTM, Penang, Malaysia, December 16-17, 2010, pp-15.

Md. Sakinul Islam, Rozita Yusoff, Brahim Si Ali*, Degradation reaction of Amines and Alkanolamines in sour Gas Processing Plant, International Conference on Sustainable Mobility 2010, (ICSM2010), UTM, Malaysia December 1-3, 2010.

Others Publications

Mook, W. T., Chakrabarti, M. H., Aroua, M. K., Khan, G. M. A., Ali, B. S., **Islam, M. S.**, and Hassan, M. A. A., Removal of total ammonia nitrogen (TAN), nitrate and total organic carbon (TOC) from aquaculture waste water using electrochemical technology: A review, Desalination (2011), doi:10.1016/j.desal.2011.09.029. **[ISI]**

M. S. Islam, R. Yusoff and B. S. Ali, Role of acid and heat stable salt in the degradation process of alkanolamine during sour gas sweetening process**,** Engineering e-Transaction (ISSN 1823-6379), Electronic Journal of University of Malaya (EJUM), Vol. 5, No. 2, December 2010, pp 53-60.

M. S. Islam, R. Yusoff and B. S. Ali, Degradation studies of amines and alkanolamines during CO_2 absorption and stripping system, Engineering e-Transaction (ISSN 1823-6379), Electronic Journal of University of Malaya (EJUM) Vol. 5, No. 2, December 2010, pp 97-109.

Mohammed Harun Chakrabarti, Mehmood Ali, Jafar Nazir Usmani, Nasim Ahmed Khan, Diya'uddeen Basheer Hasan, **Md. Sakinul Islam**, Abdul Aziz Abdul Raman, Rozita Yusoff and Mohammad Faisal Irfan. Status of biodiesel research and development in Pakistan, Renewable & Sustainable Energy Reviews, 16 (2012), pp. 4396-4405 **[ISI]**

Muhammad Saleem, Mohammed Harun Chakrabarti, Diya'uddeen Basheer Hasan, **Md. Sakinul Islam**, Rozita Yusoff, Sayed Ahmad Hajimolana, Mohd. Azlan Hussain, Gazi Md. Arifuzzaman Khan and Brahim Si Ali, On Site Electrochemical Production of Sodium Hypochlorite Disinfactant for a Power Plant Utilizing Seawater, Int. J. Electrochem. Sci., 7(2012): pp. 3929-3938. **[ISI]**

APPENDIX K: AUTHOR VITA

Mr. Md. Sakinul Islam was born on 18 August, 1979 in Village- Nando, P.O- Walia, P.S- Lalpur, Natore, Bangladesh to Festus Mr. Md. Year Uddin and Mrs. Sahera Begum. He graduated with a Bachelor of Science and Masters of Science degrees in Applied Chemistry and Chemical Technology with excellent academic background from Islamic University, Kushtia 7003, Bangladesh in 2003 and 2005 respectively. After a year of teaching service, he entered as an MPhil researcher in the Department of Chemistry, under the Faculty of Engineering in BUET, Dhaka, Bangladesh and finished his research on June, 2009. The MPhil degree was awarded on October 25, 2011. During his MPhil Studies in June, 2009 he was received an offer to join in MEngSc program at the University of Malaya, Kuala Lumpur, Malaysia and started the degree in July, 2009 under the scholastic supervision of Dr. Brahim Si Ali and Dr. Rozita Yusoff in the Dept. of Chemical Engineering, Faculty of Engineering.

This MEngSc thesis was typed by the author and the university is fully concern about this hypothesis which entitled as:

"CHARACTERIZATION OF DEGRADATION PRODUCTS OF ACTIVATED DIETHANOLAMINE AND METHYLDIETHANOLAMINE DURING CARBON DIOXIDE ABSORPTION AND DESORPTION PROCESSES"

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